

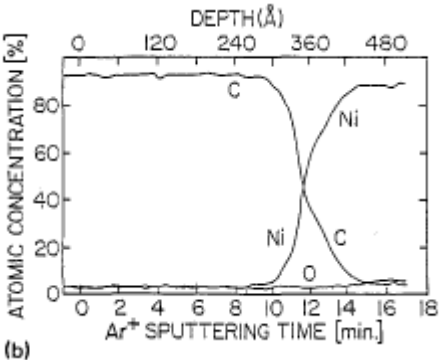
EXHIBIT A

§ 102 REFERENCES COVERING CLAIMS

'086 Patent	J. Vac. Sci. Tech. A, 6(3), pp. 1788-92 (1988); “Chemically bonded diamondlike films from ion-beam deposition” by Kasi, Kang, and Rabalais (“Kasi—VSTA”)
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The Kasi-VSTA reference was published in 1988. This is greater than one year before the '086 patent was filed on Jun. 14, 1994.</p> <p>Elements below show hard-carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>We have recently demonstrated¹ the deposition of thin diamondlike films from $^{12}\text{C}^+$ ion beams with first proof of chemical bonding to the underlying metal substrate in the form of a carbide. (Kasi-VSTA 1788).</p> <p>C^+ deposition has been performed on Ni(111), Si(100), Ta, W, and Au surfaces. No apparent dependence on the substrate surface was noticed with the host of spectroscopic techniques employed, with the exception that the C^+ dose requirements for formation of the structures did differ for the different substrates. (Kasi-VSTA 1788).</p> <div data-bbox="776 1430 1218 1789" data-label="Figure"> </div> <p>FIG. 2. (a) Phase diagram for C^+ deposition on Ni(111) as a function of C^+ ion dose and energy. Regions A, B, and C</p>

'086 Patent	J. Vac. Sci. Tech. A, 6(3), pp. 1788-92 (1988); “Chemically bonded diamondlike films from ion-beam deposition” by Kasi, Kang, and Rabalais (“Kasi—VSTA”)
	correspond to carbon films with AES line shapes of Figs. 1 (a), 1 (b), and 1 (c), respectively. (b) Depth concentration profile using 3-keV Ar ⁺ ions for a diamondlike film deposited from 75-eV C ⁺ on Ni(111). (Kasi-VSTA 1789).
an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and	<p>C⁺ deposition has been performed on Ni(111), Si(100), Ta, W, and Au surfaces. No apparent dependence on the substrate surface was noticed with the host of spectroscopic techniques employed, with the exception that the C⁺ dose requirements for formation of the structures did differ for the different substrates. (Kasi-VSTA 1788).</p> <p>The initial monolayer of the deposited film is in the form of a carbide layer which is chemically bonded to the substrate atoms. Over the next several layers deposited, the film evolves gradually through intermediate structures into a diamondlike structure. A phase diagram, prepared as C⁺ ion dose versus C⁺ kinetic energy E_k, shows the regions of the different structures. The optimum C⁺ energy range for formation of the diamond like structure is 30-175 eV. Below 10 eV the final diamondlike structure has not been attained and above 180 eV there is a sharp increase in the dose required to attain this final structure. Properties of the film, measured <i>in situ</i>, are mentioned. (Kasi-VSTA 1788, Abstract)</p> <div data-bbox="776 1409 1218 1770"> </div> <p>(b)</p> <p>FIG. 2. (a) Phase diagram for C⁺ deposition on Ni(111) as a function of C⁺ ion dose and energy. Regions A, B, and C correspond to carbon films with AES line shapes of Figs. 1</p>

'086 Patent	J. Vac. Sci. Tech. A, 6(3), pp. 1788-92 (1988); “Chemically bonded diamondlike films from ion-beam deposition” by Kasi, Kang, and Rabalais (“Kasi—VSTA”)
	<p>(a), 1 (b), and 1 (c), respectively. (b) Depth concentration profile using 3-keV Ar⁺ ions for a diamondlike film deposited from 75-eV C⁺ on Ni(111). (Kasi-VSTA 1789).</p> <p>Low-energy mass-selected C⁺ ion beams are used to deposit thin carbon films on surfaces of Si (100) and Ni (111) in an UHV environment at room temperature. . .The initial monolayer of the deposited film is in the form of a carbide layer which is chemically bonded to the substrate atoms. Over the next several layers deposited, the film evolves gradually through intermediate structures into a diamondlike structure. (Kasi-VSTA 1788).</p>
a hard carbon film arranged on said intermediate layer.	<p>Preparation of thin films by energetic particle bombardment has been a focus of recent research. Growth of films in metastable phases of superhard materials such as diamond has been actively pursued due to the various novel uses for such films. Their extreme hardness finds use as abrasion resistant coatings, while their excellent insulating characteristics coupled with the high thermal conductivity prompt applications in microelectronics. (Kasi-VSTA 1788).</p> <p>We have recently demonstrated¹ the deposition of thin diamondlike films from ¹²C⁺ ion beams with first proof of chemical bonding to the underlying metal substrate in the form of a carbide. (Kasi-VSTA 1788).</p> <div data-bbox="776 1482 1218 1843" data-label="Figure"> </div> <p>(b)</p> <p>FIG. 2. (a) Phase diagram for C⁺ deposition on Ni(111) as a</p>

'086 Patent	J. Vac. Sci. Tech. A, 6(3), pp. 1788-92 (1988); “Chemically bonded diamondlike films from ion-beam deposition” by Kasi, Kang, and Rabalais (“Kasi—VSTA”)
	function of C^+ ion dose and energy. Regions A, B, and C correspond to carbon films with AES line shapes of Figs. 1 (a), 1 (b), and 1 (c), respectively. (b) Depth concentration profile using 3-keV Ar^+ ions for a diamondlike film deposited from 75-eV C^+ on Ni(111). (Kasi-VSTA 1789).
<u>Claim 26</u>	
The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.	<p>Film thickness estimates provided, by the ellipsometry measurements were in the range 120-145 Å. (Kasi-VSTA 1791).</p>  <p>(b)</p> <p>FIG. 2. (a) Phase diagram for C^+ deposition on Ni(111) as a function of C^+ ion dose and energy. Regions A, B, and C correspond to carbon films with AES line shapes of Figs. 1 (a), 1 (b), and 1 (c), respectively. (b) Depth concentration profile using 3-keV Ar^+ ions for a diamondlike film deposited from 75-eV C^+ on Ni(111). (Kasi-VSTA 1789).</p>
<u>Claim 27</u>	
The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.	Film thickness estimates provided by the ellipsometry measurements were in the range of 120-145 Å. (Kasi-VSTA 1791).

<p>'086 Patent</p>	<p>J. Vac. Sci. Tech. A, 6(3), pp. 1788-92 (1988); “Chemically bonded diamondlike films from ion-beam deposition” by Kasi, Kang, and Rabalais (“Kasi—VSTA”)</p>
	<div data-bbox="776 352 1218 709" data-label="Figure"> </div> <p>(b)</p> <p>FIG. 2. (a) Phase diagram for C^+ deposition on Ni(111) as a function of C^+ ion dose and energy. Regions A, B, and C correspond to carbon films with AES line shapes of Figs. 1 (a), 1 (b), and 1 (c), respectively. (b) Depth concentration profile using 3-keV Ar^+ ions for a diamondlike film deposited from 75-eV C^+ on Ni(111).</p> <p>(Kasi-VSTA 1789).</p>
<p><u>Claim 28</u></p>	
<p>The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.</p>	<p>Preparation of thin films by energetic particle bombardment has been a focus of recent research. Growth of films in metastable phases of superhard materials such as diamond has been actively pursued due to the various novel uses for such films. Their extreme hardness finds use as abrasion resistant coatings, while their excellent insulating characteristics coupled with the high thermal conductivity prompt applications in microelectronics. (Kasi-VSTA 1788).</p> <p>We have recently demonstrated¹ the deposition of thin diamondlike films from $^{12}C^+$ ion beams with first proof of chemical bonding to the underlying metal substrate in the form of a carbide. (Kasi-VSTA 1788).</p> <p>Preparation of thin films by energetic particle bombardment has been a focus of recent research. Growth of films in metastable phases of superhard materials such as diamond has been actively pursued due to the various novel uses for such films. (Kasi-VSTA 1788).</p>

'086 Patent	J. Vac. Sci. Tech. A, 6(3), pp. 1788-92 (1988); “Chemically bonded diamondlike films from ion-beam deposition” by Kasi, Kang, and Rabalais (“Kasi—VSTA”)
	<p>Low-energy mass-selected C⁺ ion beams are used to deposit thin carbon films on surfaces of Si (100) and Ni (111) in an UHV environment at room temperature. . .The initial monolayer of the deposited film is in the form of a carbide layer which is chemically bonded to the substrate atoms. Over the next several layers deposited, the film evolves gradually through intermediate structures into a diamondlike structure... The optimum C⁺ energy range for formation of the diamondlike structure is 30-175 eV. (Kasi-VSTA 1788).</p>

'086 Patent	U.S. Patent No. 4,992,298 ("298 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The '298 patent was issued on Feb. 12, 1991. This is greater than one year before the '086 patent was filed on Jun. 14, 1994.</p> <p>Elements below show hard-carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>The term "ballistically alloyed" describes a process of firmly adhering a layer onto a substrate by bombardment of the substrate surface with high energy particles that become physically mixed and/or chemically bonded within the substrate surface. The resulting effect is to grow a surface layer having a thickness which extends not only above the immediate substrate surface but also extends into the substrate surface a short distance in a manner similar to a diffusion bonded layer. ('298 patent at 4:15-24).</p> <p>The resultant coated films range in thickness typically from about 100-200,000 Å, and for most applications from about 1000-20,000 Å. Although the process is particularly suitable for forming a variety of desired diamond and diamond-like films upon the surface of the substrate, a wide variety of other hard films such as nitrides, borides, carbides, oxides and the like can also be so deposited onto a desired substrate. It is, of course, apparent to one skilled in the art how changing the particular sputtered materials and/or reactive or inert gases, as well as the various energy levels of the beams, can make the resulting films morphologies different. ('298 patent at 4:54-65).</p> <p>Additionally, the process is suitable for treating an extremely wide variety of substrates, such as metals, plastics, glasses, ceramics and the like, whereas most other prior art systems are quite limited with respect to the substrates which can be treated. ('298 patent at 4:66-5:2).</p> <p>Using the same apparatus as in Example 1, a metal mold used for molding of precision glass lense is mounted to platen 15 in section 12 of chamber 10. The mold is fabricated from a nickel-based Inconel 718 alloy. The molding surface of the mold is highly polished and optically reflective. Using the same precleaning, ion beam mixing, and film growth procedures and process parameters, a continuous polycrystalline diamond film is first ballistically alloyed into, and next grown on the molding surface of the mold to a thickness of</p>

'086 Patent	U.S. Patent No. 4,992,298 ("298 Patent")
	<p>approximately 1000 angstroms at a rate of 2 angstroms per minute. No change in the precision polished surface of the mold was evidenced due to the presence of the grown diamond film layer. The diamond film thus deposited on the mold acts both as a hard protective layer exhibiting much improved abrasive wear resistance, and also as a chemically inert layer reducing chemical attack of the critical molding surface by the molten glass. ('298 patent at 6:62-7:11).</p>
<p>an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and</p>	<p>More particularly, the invention relates to a method which simultaneously utilizes a low energy sputtered beam and a high energy bombarding beam to produce thin, pure, stress-reduced hard films such as polycrystalline diamond which can be bonded to a wide variety of substrates; the deposited coatings being bonded to the substrate within a thin, boundary zone in which the deposited layer has physically mixed and/or chemically bonded onto the substrate. ('298 patent at 1:11-20).</p> <p>Simultaneously with the aforementioned bombardment of the substrate 16 with beam 32, ion beam source 20 generates a different beam 18, which is a high energy beam of inert atoms, i.e., argon, neon, krypton and xenon, having energies ranging from about 0.5-100 KeV, preferably 0.5-5.0 KeV. This high energy beam strikes the substrate 16 concurrently with the initial deposition of the sputtered carbon or other low energy atoms present in beam 32 and bombards the substrate 16 surface until a ballistically alloyed layer ranging in thickness from about 10-2000 Å preferably about 10-20 Å has been bonded onto the substrate. The term "ballistically alloyed" describes a process of firmly adhering a layer onto a substrate by bombardment of the substrate surface with high energy particles that become physically mixed and/or chemically bonded within the substrate surface. The resulting effect is to grow a surface layer having a thickness which extends not only above the immediate substrate surface but also extends into the substrate surface a short distance in a manner similar to a diffusion bonded layer. Thus, the net effect of the high energy bombardment while simultaneously depositing a low energy sputtered film is to create a ballistically bonded, thin, preferably hydrogen-free, reduced in internal stress, amorphous, crystalline or polycrystalline layer of a pure substance firmly alloyed into the substrate. The ballistic alloying occurs in a thin, e.g., from 10-2000 Å and preferably 10 to 20 Å boundary zone in which the sputtered layer has become physically mixed and/or chemically bonded with the substrate to produce a strong, effective bond. ('298 patent at 4:4-34).</p>

'086 Patent	U.S. Patent No. 4,992,298 ("298 Patent")
	<p>The dual ion beam ballistic alloying process has an additional advantage in that it allows a high degree of control with respect to such variables as the initial surface cleaning of the target substrate, the arrival of the deposited carbon or other sputtered material onto the substrate surface, the concentration and depth profile of the initial ballistically bonded zone in the substrate surface and the careful control of the resultant diamond or other film morphology during the later growth phase upon the substrate. ('298 patent at 5:47-56).</p> <p>10. This produces a sputtered beam 32 consisting of carbon atoms. The carbon atoms arriving at the plastic lens surface are ion beam mixed into the surface of the lens for approximately ½ hour. The voltage of ion beam 18 is then reduced to approximately 150 volts and the current level of ion beam 18 is adjusted to 10 ma to allow the growth of SP₃ bonded polycrystalline diamond films on the plastic lens surface. The 10 ma for ion beam 18 is adjusted by monitoring film growth rates with thin film sensor 40. The temperature rise in the lens remains below 150 degrees F. during all processing steps. A continuous polycrystalline diamond film, initially ion beam mixed into the surface of the plastic lens, is grown on the lens to a thickness of 1000 angstroms at a rate of 2 angstroms per minute. The diamond film thus deposited on the surface of the plastic lens acts as a hard protective layer which increases the resistance of the lens to scratching and abrasive wear. ('298 patent at 6:41-58).</p>
a hard carbon film arranged on said intermediate layer.	<p>The invention discloses a dual ion beam ballistic alloying process for forming a film such as diamond onto a substrate, which comprises the steps of: (a) cleaning the surface of the substrate with a first energy beam of inert atoms; (b) depositing a layer of a desired non-hydrocarbon substance on the substrate with a low energy, sputtered atomic beam; (c) simultaneously exposing the substrate to said first energy beam of inert atoms with a high energy to grow a ballistically alloyed layer having a thickness of about 10-2000 Å; and (d) reducing the energy level of the first, high energy beam to cause the growth of the layer of said substance on said substrate to a final desired thickness. ('298 patent at Abstract).</p> <p>The dual ion beam ballistic alloying process has an additional advantage in that it allows a high degree of control with respect to such variables as the initial surface cleaning of the target substrate,</p>

'086 Patent	U.S. Patent No. 4,992,298 ("298 Patent")
	<p>the arrival of the deposited carbon or other sputtered material onto the substrate surface, the concentration and depth profile of the initial ballistically bonded zone in the substrate surface and the careful control of the resultant diamond or other film morphology during the later growth phase upon the substrate. (298 patent at 5:47-56).</p> <p>More particularly, the invention relates to a method which simultaneously utilizes a low energy sputtered beam and a high energy bombarding beam to produce thin, pure, stress-reduced hard films such as polycrystalline diamond which can be bonded to a wide variety of substrates; the deposited coatings being bonded to the substrate within a thin, boundary zone in which the deposited layer has physically mixed and/or chemically bonded onto the substrate. (298 patent at 1:11-20).</p> <p>Although the process is particularly suitable for forming a variety of desired diamond and diamond-like films upon the surface of the substrate, a wide variety of other hard films such as nitrides, borides, carbides, oxides and the like can also be so deposited onto a desired substrate. (298 patent at 4:56-61).</p> <p>With respect to the preferred diamond coatings of the invention, the process, as indicated above, can both accurately control the thickness of the deposited diamond film, and also the physical characteristics of the diamond films which are so deposited. More particularly, a wide variety of diamond films which exhibit predominantly SP_3 bonding or mixtures of SP_2 and SP_3 bonded carbon can be produced. (298 patent at 5:14-21).</p>
<u>Claim 26</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p>The invention discloses a dual ion beam ballistic alloying process for forming a film such as diamond onto a substrate, which comprises the steps of: (a) cleaning the surface of the substrate with a first energy beam of inert atoms; (b) depositing a layer of a desired non-hydrocarbon substance on the substrate with a low energy, sputtered atomic beam; (c) simultaneously exposing the substrate to said first energy beam of inert atoms with a high energy to grow a ballistically alloyed layer having a thickness of about 10-2000 Å; and (d) reducing the energy level of the first, high energy beam to cause the growth of the layer of said substance on said substrate to a final desired thickness.</p>

'086 Patent	U.S. Patent No. 4,992,298 ("298 Patent")
	<p>('298 patent at Abstract).</p> <p>Using the same precleaning, ion beam mixing, and film growth procedures and process parameters, a continuous polycrystalline diamond film is first ballistically alloyed into, and next grown on the molding surface of the mold to a thickness of approximately 1000 angstroms at a rate of 2 angstroms per minute.</p> <p>('298 patent at 6:67-7:5).</p>
<u>Claim 27</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.</p>	<p>The invention discloses a dual ion beam ballistic alloying process for forming a film such as diamond onto a substrate, which comprises the steps of: (a) cleaning the surface of the substrate with a first energy beam of inert atoms; (b) depositing a layer of a desired non-hydrocarbon substance on the substrate with a low energy, sputtered atomic beam; (c) simultaneously exposing the substrate to said first energy beam of inert atoms with a high energy to grow a ballistically alloyed layer having a thickness of about 10-2000 Å; and (d) reducing the energy level of the first, high energy beam to cause the growth of the layer of said substance on said substrate to a final desired thickness.</p> <p>('298 patent at Abstract).</p> <p>Using the same precleaning, ion beam mixing, and film growth procedures and process parameters, a continuous polycrystalline diamond film is first ballistically alloyed into, and next grown on the molding surface of the mold to a thickness of approximately 1000 angstroms at a rate of 2 angstroms per minute.</p> <p>('298 patent at 6:67-7:5).</p>
<u>Claim 28</u>	
<p>The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.</p>	<p>The invention discloses a dual ion beam ballistic alloying process for forming a film such as diamond onto a substrate, which comprises the steps of: (a) cleaning the surface of the substrate with a first energy beam of inert atoms; (b) depositing a layer of a desired non-hydrocarbon substance on the substrate with a low energy, sputtered atomic beam; (c) simultaneously exposing the substrate to said first energy beam of inert atoms with a high energy to grow a ballistically alloyed layer having a thickness of about 10-2000 Å; and (d) reducing the energy level of the first, high energy beam to cause the growth of the layer of said substance on said substrate to a final desired thickness.</p> <p>('298 patent at Abstract).</p>

'086 Patent	U.S. Patent No. 4,992,298 ("298 Patent")
	<p>More particularly, the invention relates to a method which simultaneously utilizes a low energy sputtered beam and a high energy bombarding beam to produce thin, pure, stress-reduced hard films such as polycrystalline diamond which can be bonded to a wide variety of substrates; the deposited coatings being bonded to the substrate within a thin, boundary zone in which the deposited layer has physically mixed and/or chemically bonded onto the substrate. ('298 patent at 1:10-19).</p> <p>The resultant coated films range in thickness typically from about 100-200,000 Å, and for most applications from about 1000-20,000 Å. Although the process is particularly suitable for forming a variety of desired diamond and diamond-like films upon the surface of the substrate, a wide variety of other hard films such as nitrides, borides, carbides, oxides and the like can also be so deposited onto a desired substrate. It is, of course, apparent to one skilled in the art how changing the particular sputtered materials and/or reactive or inert gases, as well as the various energy levels of the beams, can make the resulting films morphologies different. ('298 patent at 4:54-65).</p> <p>The invention comprises, in a second aspect, an article comprising a substrate having ballistically alloyed thereon a thin, reduced in internal stress, amorphous, crystalline or polycrystalline layer of a desired substance; the ballistic alloying occurring within a boundary zone in which the thin layer has physically mixed and/or chemically bonded with the substrate. ('298 patent at 2:25-31)</p> <p>With respect to the preferred diamond coatings of the invention, the process, as indicated above, can both accurately control the thickness of the deposited diamond film, and also the physical characteristics of the diamond films which are so deposited. More particularly, a wide variety of diamond films which exhibit predominantly SP₃ bonding or mixtures of SP₂ and SP₃ bonded carbon can be produced. ('298 patent at 5:14-21).</p>

'086 Patent	U.S. Patent No. 5,064,682 ("682 Patent")
Claim 25	
A hard-carbon-film coated substrate comprising:	<p>The '682 patent was issued on Feb. 12, 1991. This is greater than one year before the '086 patent was filed on Jun. 14, 1994.</p> <p>Elements below show hard-carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>A method of forming a pseudo-diamond film on a base body, the method comprising a first step of irradiating carbon ions onto a surface of a base body from an assisting ion gun to form a mixture layer comprising base body material atoms and carbon atoms; a second step of simultaneously vapor-depositing the carbon atoms from a vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the mixture layer to form pseudo-diamond cores on the mixtures layer; and a third step of vapor-depositing carbon atoms from the vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the pseudo-diamond cores to form a pseudo-diamond film on the pseudodiamond cores. ('682 patent at Abstract).</p> <p>The base body may be formed of a material selected from the group consisting of stainless steel, carbon steel, electrocasted nickel, copper, copper alloys, ceramics, aluminum, aluminum alloys, magnesium, magnesium alloys and reinforced plastics. ('682 patent at 1:47-51).</p>
an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and	<p>A method of forming a pseudo-diamond film on a base body, the method comprising a first step of irradiating carbon ions onto a surface of a base body from an assisting ion gun to form a mixture layer comprising base body material atoms and carbon atoms; a second step of simultaneously vapor-depositing the carbon atoms from a vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the mixture layer to form pseudo-diamond cores on the mixtures layer; and a third step of vapor-depositing carbon atoms from the vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the pseudo-diamond cores to form a pseudo-diamond film on the pseudodiamond cores. ('682 patent at Abstract).</p> <p>The above object is also fulfilled by a method of forming a pseudo-diamond film using a vacuum deposition and ion irradiation apparatus including a rotatable base body holder, a vapor deposition source and an assisting ion gun in a chamber, the method comprising a first step of irradiating carbon ions onto a surface of a base body from an assisting ion gun to form a mixture layer comprising base</p>

'086 Patent	U.S. Patent No. 5,064,682 ("682 Patent")
	<p>body material atoms and carbon atoms while rotating a base body holder; a second step of simultaneously vapor-depositing the carbon atoms from a vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the mixture layer while rotating the base body holder to form pseudo-diamond cores on the mixture layer; and a third step of vapor-depositing carbon atoms from the vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the pseudo-diamond cores while rotating the base body holder to form a pseudodiamond film on the pseudo-diamond cores.</p> <p>The above object is also fulfilled by a method of forming a pseudo-diamond film using a vacuum deposition and ion irradiation apparatus including a rotatable base body holder, a vapor deposition source, a first assisting ion gun for high energy acceleration and a second assisting ion gun for low energy acceleration in a chamber, the method comprising a first step of irradiating carbon ions onto a surface of a base body from a first assisting ion gun to form a mixture layer comprising base body material atoms and carbon atoms; a second step of irradiating inert gas ions such as argon ions from a second assisting ion gun onto the mixture layer to roughen a surface of the mixture layer; a third step of simultaneously irradiating carbon ions from the first assisting ion gun and irradiating a mixture of hydrogen ions and inert gas ions such as argon ions from the second assisting ion gun onto the mixture layer to form pseudo-diamond cores on the mixture layer; and a fourth step of simultaneously driving a vapor deposition source to vapor-deposit carbon atoms and irradiating hydrogen ions and inert gas ions such as argon ions from the second assisting ion gun onto the pseudo diamond cores to form a pseudo-diamond film on the pseudo-diamond cores.</p> <p>According to the above, a mixture layer is first formed on a base body, and then a pseudo-diamond film is formed on the mixture layer. Since the mixture layer has components both of the film and the base body, the film is adhered on the base body strongly. This strong adhesion greatly improves tenacity and hardness of the base body. ('682 patent at 2:35-3:16).</p>
a hard carbon film arranged on said intermediate layer.	A method of forming a pseudo-diamond film on a base body, the method comprising a first step of irradiating carbon ions onto a surface of a base body from an assisting ion gun to form a mixture layer comprising base body material atoms and carbon atoms; a second step of simultaneously vapor-depositing the carbon atoms

'086 Patent	U.S. Patent No. 5,064,682 ("682 Patent")
	<p>from a vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the mixture layer to form pseudo-diamond cores on the mixtures layer; and a third step of vapor-depositing carbon atoms from the vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the pseudo-diamond cores to form a pseudo-diamond film on the pseudodiamond cores. ('682 patent at Abstract).</p> <p>The above object is also fulfilled by a method of forming a pseudo-diamond film using a vacuum deposition and ion irradiation apparatus including a rotatable base body holder, a vapor deposition source and an assisting ion gun in a chamber, the method comprising a first step of irradiating carbon ions onto a surface of a base body from an assisting ion gun to form a mixture layer comprising base body material atoms and carbon atoms while rotating a base body holder; a second step of simultaneously vapor-depositing the carbon atoms from a vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the mixture layer while rotating the base body holder to form pseudo-diamond cores on the mixture layer; and a third step of vapor-depositing carbon atoms from the vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the pseudo-diamond cores while rotating the base body holder to form a pseudo diamond film on the pseudo-diamond cores. The above object is also fulfilled by a method of forming a pseudo-diamond film using a vacuum deposition and ion irradiation apparatus including a rotatable base body holder, a vapor deposition source, a first assisting ion gun for high energy acceleration and a second assisting ion gun for low energy acceleration in a chamber, the method comprising a first step of irradiating carbon ions onto a surface of a base body from a first assisting ion gun to form a mixture layer comprising base body material atoms and carbon atoms; a second step of irradiating inert gas ions such as argon ions from a second assisting ion gun onto the mixture layer to roughen a surface of the mixture layer; a third step of simultaneously irradiating carbon ions from the first assisting ion gun and irradiating a mixture of hydrogen ions and inert gas ions such as argon ions from the second assisting ion gun onto the mixture layer to form pseudo-diamond cores on the mixture layer; and a fourth step of simultaneously driving a vapor deposition source to vapor-deposit carbon atoms and irradiating hydrogen ions and inert gas ions such as argon ions from the second assisting ion gun onto the pseudo diamond cores to form a pseudo-diamond film on the pseudo-diamond cores.</p> <p>According to the above, a mixture layer is first formed on a base</p>

'086 Patent	U.S. Patent No. 5,064,682 ("682 Patent")
	<p>body, and then a pseudo-diamond film is formed on the mixture layer. Since the mixture layer has components both of the film and the base body, the film is adhered on the base body strongly. This strong adhesion greatly improves tenacity and hardness of the base body. ('682 patent at 2:35-3:16).</p>
<u>Claim 26</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p>In this way, the mixture layer 6 having a thickness of, for example, 0.1 μm is formed on the surface of the edge base 3 (FIG. 3a). ('682 patent at 4:18-20).</p> <p>Then, the current density and the acceleration voltage are drastically reduced to 2mA/cm² and 200eV, respectively, and are kept at these levels for approx. 2 minutes while the edge base holder 2 is rotated (FIG. 4). As a result, the a uniform film is formed on the cores 9 in a uniform quality (FIG. 3c). The film forming speed is 250Å/min., and the thickness of the film is approx. 0.33 μm. ('682 patent at 5:10-17).</p> <p>Carbon ions are irradiated from the high energy ion gun 10 to the surface of the edge base 3 with an acceleration voltage of 1 to 100keV, while the edge base holder 2 is rotated in the direction of the arrow of FIG. 1 at 10 to 20 rpm, thereby to form the mixture layer 6 having a thickness of, for example, 0.1 μm (FIG. 9a). ('682 patent at 5:45-50).</p>
<u>Claim 27</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.</p>	<p>In this way, the mixture layer 6 having a thickness of, for example, 0.1 μm is formed on the surface of the edge base 3 (FIG. 3a). ('682 patent at 4:18-20).</p> <p>Then, the current density and the acceleration voltage are drastically reduced to 2mA/cm² and 200eV, respectively, and are kept at these levels for approx. 2 minutes while the edge base holder 2 is rotated (FIG. 4). As a result, the a uniform film is formed on the cores 9 in a uniform quality (FIG. 3c). The film forming speed is 250Å/min., and the thickness of the film is approx. 0.33 μm. ('682 patent at 5:10-17).</p> <p>Carbon ions are irradiated from the high energy ion gun 10 to the surface of the edge base 3 with an acceleration voltage of 1 to 100keV, while the edge base holder 2 is rotated in the direction of the arrow of FIG. 1 at 10 to 20 rpm, thereby to form the mixture layer 6 having a thickness of, for example, 0.1 μm (FIG. 9a).</p>

'086 Patent	U.S. Patent No. 5,064,682 ("682 Patent")
	('682 patent at 5:45-50). .
Claim 28	
<p>The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.</p>	<p>A method of forming a pseudo-diamond film on a base body, the method comprising a first step of irradiating carbon ions onto a surface of a base body from an assisting ion gun to form a mixture layer comprising base body material atoms and carbon atoms; a second step of simultaneously vapor-depositing the carbon atoms from a vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the mixture layer to form pseudo-diamond cores on the mixtures layer; and a third step of vapor-depositing carbon atoms from the vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the pseudo-diamond cores to form a pseudo-diamond film on the pseudodiamond cores. ('682 patent at Abstract).</p> <p>The above object is also fulfilled by a method of forming a pseudo-diamond film using a vacuum deposition and ion irradiation apparatus including a rotatable base body holder, a vapor deposition source and an assisting ion gun in a chamber, the method comprising a first step of irradiating carbon ions onto a surface of a base body from an assisting ion gun to form a mixture layer comprising base body material atoms and carbon atoms while rotating a base body holder; a second step of simultaneously vapor-depositing the carbon atoms from a vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the mixture layer while rotating the base body holder to form pseudo-diamond cores on the mixture layer; and a third step of vapor-depositing carbon atoms from the vapor deposition source and irradiating hydrogen ions from the assisting ion gun onto the pseudo-diamond cores while rotating the base body holder to form a pseudo diamond film on the pseudo-diamond cores. The above object is also fulfilled by a method of forming a pseudo-diamond film using a vacuum deposition and ion irradiation apparatus including a rotatable base body holder, a vapor deposition source, a first assisting ion gun for high energy acceleration and a second assisting ion gun for low energy acceleration in a chamber, the method comprising a first step of irradiating carbon ions onto a surface of a base body from a first assisting ion gun to form a mixture layer comprising base body material atoms and carbon atoms; a second step of irradiating inert gas ions such as argon ions from a second assisting ion gun onto the mixture layer to roughen a surface of the mixture layer; a third step of simultaneously irradiating carbon ions from the first assisting ion gun and irradiating a mixture of hydrogen ions and inert gas ions such as argon ions from the second assisting ion gun onto the mixture</p>

'086 Patent	U.S. Patent No. 5,064,682 ("682 Patent")
	<p>layer to form pseudo-diamond cores on the mixture layer; and a fourth step of simultaneously driving a vapor deposition source to vapor-deposit carbon atoms and irradiating hydrogen ions and inert gas ions such as argon ions from the second assisting ion gun onto the pseudo diamond cores to form a pseudo-diamond film on the pseudo-diamond cores.</p> <p>According to the above, a mixture layer is first formed on a base body, and then a pseudo-diamond film is formed on the mixture layer. Since the mixture layer has components both of the film and the base body, the film is adhered on the base body strongly. This strong adhesion greatly improves tenacity and hardness of the base body.</p> <p>('682 patent at 2:35-3:16).</p>

'086 Patent	U.S. Patent No. 5,474,816 ("816 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The '816 patent was filed in the U.S. PTO on April 16, 1993.</p> <p>Elements below show hard-carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>Suitable substrates include those which are capable of forming a carbide compound, such as silicon, aluminum, tantalum, titanium, molybdenum and chromium. In addition, tungsten carbide, tool steel, stainless steel, and certain plastics may also be used. ('816 patent at 4:8-12).</p>
an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and	<p>The substrate may optimally be coated with an intermediate layer prior to coating a substrate with amorphous diamond. The intermediate layer acts as a binder to improve the adhesion of the substrate to amorphous diamond. Suitable intermediate layers include chromium and titanium. Alternatively, a DC bias voltage of 1-5 kV may be applied to the substrate to form a diffuse interface. ('816 patent at 4:14-20).</p> <p>One object of the present invention is to provide a method for coating a substrate with an amorphous diamond film which overcomes the aforementioned problems of the related art.</p> <p>A second object of the invention is to coat a substrate with an amorphous diamond film by cooling and biasing said substrate and condensing carbon ions thereon.</p> <p>A third object of the invention is to produce an amorphous diamond film characterized by sufficient hardness and reduced intrinsic stress. ('816 patent at 1:57-67).</p> <p>A fourth object of the present invention is to provide a method for coating various instruments and tools with amorphous diamond. Yet another object of the invention is to produce an article of manufacture that has at least one surface with an amorphous diamond film coating having an intrinsic stress substantially below 6 GPa. ('816 patent at 2:1-7).</p> <p>The present invention provides a method for coating a substrate with an amorphous diamond film by cooling a substrate; biasing the substrate; and condensing carbon ions thereon. In the above process, the substrate may be cooled while carbon ions are being condensed onto said substrate. The article may be coated at room temperature or alternatively, below room temperature, depending on the coolant selected. ('816 patent at 2:15-22).</p>

'086 Patent	U.S. Patent No. 5,474,816 ("816 Patent")
	<p>Carbon ions from a source that produces a carbon ion beam in the 20 to 200 eV range are condensed onto substrates. The substrate is biased with an energy source. Preferably the energy source comprises a radio frequency generator and impedance matching network that maintains the voltage between approximately -70 and -225 volts. Biasing the substrate by itself will reduce the intrinsic stress of amorphous diamond. However, biasing and doping the substrate with dopant will further reduce the intrinsic stress. ('816 patent at 4:22-30).</p>
<p>a hard carbon film arranged on said intermediate layer.</p>	<p>Amorphous diamond films having a significant reduction in intrinsic stress are prepared by biasing a substrate to be coated and depositing carbon ions thereon under controlled temperature conditions. ('816 patent at Abstract).</p> <p>The substrate may optimally be coated with an intermediate layer prior to coating a substrate with amorphous diamond. The intermediate layer acts as a binder to improve the adhesion of the substrate to amorphous diamond. Suitable intermediate layers include chromium and titanium. Alternatively, a DC bias voltage of 1-5 kV may be applied to the substrate to form a diffuse interface. ('816 patent at 4:14-20).</p> <p>One object of the present invention is to provide a method for coating a substrate with an amorphous diamond film which overcomes the aforementioned problems of the related art.</p> <p>A second object of the invention is to coat a substrate with an amorphous diamond film by cooling and biasing said substrate and condensing carbon ions thereon.</p> <p>A third object of the invention is to produce an amorphous diamond film characterized by sufficient hardness and reduced intrinsic stress. ('816 patent at 1:57-67).</p> <p>A fourth object of the present invention is to provide a method for coating various instruments and tools with amorphous diamond.</p> <p>Yet another object of the invention is to produce an article of manufacture that has at least one surface with an amorphous diamond film coating having an intrinsic stress substantially below 6 GPa. ('816 patent at 2:1-7).</p> <p>The present invention provides a method for coating a substrate with an amorphous diamond film by cooling a substrate; biasing the substrate; and condensing carbon ions thereon. In the above process, the substrate may be cooled while carbon ions are being condensed</p>

'086 Patent	U.S. Patent No. 5,474,816 ("816 Patent")
	<p>onto said substrate. The article may be coated at room temperature or alternatively, below room temperature, depending on the coolant selected. ('816 patent at 2:15-22).</p> <p>Carbon ions from a source that produces a carbon ion beam in the 20 to 200 eV range are condensed onto substrates. The substrate is biased with an energy source. Preferably the energy source comprises a radio frequency generator and impedance matching network that maintains the voltage between approximately -70 and -225 volts. Biasing the substrate by itself will reduce the intrinsic stress of amorphous diamond. However, biasing and doping the substrate with dopant will further reduce the intrinsic stress. ('816 patent at 4:22-30).</p>
<u>Claim 26</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p>On carbide-forming materials, the adhesion is sufficient to produce thick coatings without the compressive stress causing delamination as long as the bias voltage is maintained above -120 volts during deposition. In this manner, coatings of up to 8 micrometers thick have been produced on a tungsten carbide tool bit without delamination. An amorphous diamond film greater than 8 micrometers may also be produced using the process of this invention. ('816 patent at 6:17-25).</p>
<u>Claim 27</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.</p>	<p>On carbide-forming materials, the adhesion is sufficient to produce thick coatings without the compressive stress causing delamination as long as the bias voltage is maintained above -120 volts during deposition. In this manner, coatings of up to 8 micrometers thick have been produced on a tungsten carbide tool bit without delamination. An amorphous diamond film greater than 8 micrometers may also be produced using the process of this invention. ('816 patent at 6:17-25).</p>
<u>Claim 28</u>	
<p>The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.</p>	<p>Amorphous diamond films having a significant reduction in intrinsic stress are prepared by biasing a substrate to be coated and depositing carbon ions thereon under controlled temperature conditions. ('816 patent at Abstract).</p> <p>The substrate may optimally be coated with an intermediate layer</p>

'086 Patent	U.S. Patent No. 5,474,816 ("816 Patent")
	<p>prior to coating a substrate with amorphous diamond. The intermediate layer acts as a binder to improve the adhesion of the substrate to amorphous diamond. Suitable intermediate layers include chromium and titanium. Alternatively, a DC bias voltage of 1-5 kV may be applied to the substrate to form a diffuse interface. ('816 patent at 4:14-20).</p> <p>One object of the present invention is to provide a method for coating a substrate with an amorphous diamond film which overcomes the aforementioned problems of the related art.</p> <p>A second object of the invention is to coat a substrate with an amorphous diamond film by cooling and biasing said substrate and condensing carbon ions thereon.</p> <p>A third object of the invention is to produce an amorphous diamond film characterized by sufficient hardness and reduced intrinsic stress. ('816 patent at 1:57-67).</p> <p>A fourth object of the present invention is to provide a method for coating various instruments and tools with amorphous diamond. Yet another object of the invention is to produce an article of manufacture that has at least one surface with an amorphous diamond film coating having an intrinsic stress substantially below 6 GPa. ('816 patent at 2:1-7).</p> <p>The present invention provides a method for coating a substrate with an amorphous diamond film by cooling a substrate; biasing the substrate; and condensing carbon ions thereon. In the above process, the substrate may be cooled while carbon ions are being condensed onto said substrate. The article may be coated at room temperature or alternatively, below room temperature, depending on the coolant selected. ('816 patent at 2:15-22).</p> <p>Carbon ions from a source that produces a carbon ion beam in the 20 to 200 eV range are condensed onto substrates. The substrate is biased with an energy source. Preferably the energy source comprises a radio frequency generator and impedance matching network that maintains the voltage between approximately -70 and -225 volts. Biasing the substrate by itself will reduce the intrinsic stress of amorphous diamond. However, biasing and doping the substrate with dopant will further reduce the intrinsic stress. ('816 patent at 4:22-30).</p>

'086 Patent	Rother, et al., 6 J. Mater. Res. 101-11 (Jan. 1991) ("Rother-JMR")																				
Claim 25																					
A hard-carbon-film coated substrate comprising:	<p>The Rother-JMR reference was published in January 1991. This is greater than one year before the '086 patent was filed on Jun. 14, 1994.</p> <p>Elements below show hard-carbon film.</p>																				
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>Coatings of some 10 nm up to 2.5 μm have been deposited on the substrates listed in Table I. According to the aims of this investigation, various deposition parameters have been applied (Table II). It should be noted that the deposition of well-adherent coatings with a thickness of more than 0.5 μm required an increased bias voltage of usually - 400 V during the first 20 s of the deposition cycle. After that time the required dc or dc/rf bias supply was adjusted. For that purpose, in the case of the dc/rf bias mode, the dc bias was set to -100 V and the rf power was increased subsequently until the dc substrate current was zero. The deposition of thin films in the nanometer range proceeded, however, by adjusting the required bias voltage and bias mode prior to opening of the shutter and keeping them constant during deposition.</p> <p>(Rother-JMR, 102)</p> <div><p>TABLE I. Substrate materials.</p><table><tr><th>Substrate material</th><th>Specification of the material</th><th>HV_{0.05}/GPa</th><th>α_{th}/10⁻⁶ K⁻¹</th></tr><tr><td>Silicon wafer</td><td>(111) orientation ρ_{el} = 10⁻³ Ω cm</td><td></td><td>2</td></tr><tr><td>Hardened ball bearing steel</td><td>100Cr6^a Δ 1.0 wt. % C 1.5 wt. % Cr</td><td>14</td><td>12.2</td></tr><tr><td>Stainless steel</td><td>X8Cr17^a Δ 0.08 wt. % C 17 wt. % Cr</td><td>2</td><td>10.0</td></tr><tr><td>Cemented carbide</td><td>HS 123^a Δ 78 wt. % WC 15 wt. % TiC 7 wt. % Co</td><td>18</td><td>5.5</td></tr></table><p>^a German specification. HV_{0.05} Vicker's hardness at loads of 0.05 kp, own measurements. α_{th} Thermal expansion coefficient, manufacturer's specification.</p></div> <p>(Rother-JMR, 102, Table 1)</p> <p>The substrate materials applied in our experiments are listed in Table I together with some of their relevant properties. The surfaces to be coated were polished to a medium roughness of less than 1 μm. Before mounting the substrates in the coating apparatus, a cleaning</p>	Substrate material	Specification of the material	HV _{0.05} /GPa	α _{th} /10 ⁻⁶ K ⁻¹	Silicon wafer	(111) orientation ρ _{el} = 10 ⁻³ Ω cm		2	Hardened ball bearing steel	100Cr6 ^a Δ 1.0 wt. % C 1.5 wt. % Cr	14	12.2	Stainless steel	X8Cr17 ^a Δ 0.08 wt. % C 17 wt. % Cr	2	10.0	Cemented carbide	HS 123 ^a Δ 78 wt. % WC 15 wt. % TiC 7 wt. % Co	18	5.5
Substrate material	Specification of the material	HV _{0.05} /GPa	α _{th} /10 ⁻⁶ K ⁻¹																		
Silicon wafer	(111) orientation ρ _{el} = 10 ⁻³ Ω cm		2																		
Hardened ball bearing steel	100Cr6 ^a Δ 1.0 wt. % C 1.5 wt. % Cr	14	12.2																		
Stainless steel	X8Cr17 ^a Δ 0.08 wt. % C 17 wt. % Cr	2	10.0																		
Cemented carbide	HS 123 ^a Δ 78 wt. % WC 15 wt. % TiC 7 wt. % Co	18	5.5																		

'086 Patent	Rother, et al., 6 J. Mater. Res. 101-11 (Jan. 1991) ("Rother-JMR")
	<p>procedure was applied consisting of mechanical polishing with ethanol followed by ultrasonic cleaning in trichlorethylen and a final treatment in boiling benzine.</p> <p>After pumping down the deposition chamber to a base pressure of less than 10^{-3} Pa, and prior to deposition, the substrates were sputter cleaned by operating the system for about 30 min with argon at 1 Pa and with a voltage of 600 V applied between the substrate holder and the deposition chamber. At the end of the cleaning procedure, the shutter was closed and the system was evacuated to the base pressure. (Rother-JMR, 101-102)</p>
<p>an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and</p>	<p>It should be noted that the deposition of well-adherent coatings with a thickness of more than 0.5 μm required an increased bias voltage of usually - 400 V during the first 20 s of the deposition cycle. After that time the required dc or dc/rf bias supply was adjusted. For that purpose, in the case of the dc/rf bias mode, the dc bias was set to -100 V and the rf power was increased subsequently until the dc substrate current was zero. The deposition of thin films in the nanometer range proceeded, however, by adjusting the required bias voltage and bias mode prior to opening of the shutter and keeping them constant during deposition. (Rother-JMR, 102)</p> <p>The arc discharge was ignited at a pressure of 10^{-3} Pa and the arc current was maintained at 125 A. The heat load of the cathode caused a short-time increase of the working pressure to 10^{-1} Pa. At a pressure of 10^{-3} Pa the deposition is performed by adjusting the bias voltage to a suitable value and opening the shutter. At a distance of 30 cm between cathode and substrate holder an average substrate current density of $\approx 6 \text{ mA cm}^{-2}$ was measured corresponding to a growth rate of $0.1 \mu\text{m min}^{-1}$.⁹ By varying the arc current and the substrate position, the deposition may be operated at growth rates from 0.01 to $0.5 \mu\text{m min}^{-1}$. Film-forming particles are carbon ions and graphitic fragments of the cathode material. (Rother-JMR, 102)</p>
<p>a hard carbon film arranged on said intermediate layer.</p>	<p>Carbon films deposited by a modified dc cathodic arc technique were characterized by several analytical methods. The coating consist of two constituents originating from process characteristics of the technique applied. Small fragments of graphite are embedded in a matrix material of an amorphous structure with diamond-like short range order. The coating exhibit friction and wear reducing properties.</p>

'086 Patent	Rother, et al., 6 J. Mater. Res. 101-11 (Jan. 1991) ("Rother-JMR")
	<p>(Rother-JMR, Abstract)</p> <p>CADT-deposited carbon coatings are reported to exhibit exceptional hardness and high electrical resistivity.^{1,7} The structure of carbon thin films deposited by dc CADT with particle separation is described in terms of a diamond-like short-range order of carbon atoms.^{1,8}</p> <p>(Rother-JMR, 101)</p> <p>The combination of graphitic and diamond-like carbon phases proves to be a suitable coating materials for mechanically stressed elements. It may also be expected that the rough carbon surface is eligible for the surface finish of medical implants.</p> <p>(Rother-JMR, 110)</p> <p>2. Matrix material</p> <p>Matrix material of the CADT-deposited c-C coatings was analyzed in the form of thin film areas by electron transmission techniques. In the course of the investigation of the films a separation of the matrix constituent could be achieved by careful adjustment of the areas under investigation.</p> <p>ED experiments proved the amorphous structure of the c-C matrix material. Notwithstanding varying deposition parameters, the Diff(<i>r</i>) function computed from our ED data shows relatively sharp oscillations up to $r \approx 7 \text{ \AA}$, which indicates a near order extending over regions up to 14 \AA in diameter. Matrix materials of films deposited at bias voltages between -50 and</p> <p>(Rother-JMR, 105)</p> <p>-100 V, however, exhibit the most diamond-like structure and will be considered in the present paper in more detail. Table IV shows interatomic distances, coordination numbers, and mass density values obtained for our c-C matrix material in comparison with other carbon modifications. Figure 6 is a typical Diff(<i>r</i>) function of matrix material deposited at -100 V bias voltage. The first distinctly marked interatomic distance $r_1 = 1.51 \pm 0.05 \text{ \AA}$ corresponds closely to the value given for sp^3 bonds. The next maximum at $r_2 = 2.46 \pm 0.05 \text{ \AA}$ characterizes the second coordination sphere of carbon atoms being of a lower value than in crystalline diamond.</p> <p>(Rother-JMR, 106)</p> <p>Carbon coatings deposited by the dc cathodic arc technique consist of two substantially different constituents. The analysis of these two</p>

'086 Patent	Rother, et al., 6 J. Mater. Res. 101-11 (Jan. 1991) ("Rother-JMR")
	<p>substances shows correspondence to data given in the literature and to well-established ideas of the film growth from free atoms and particles.</p> <p>In particular, the macroscopic particles in the coatings were determined to be of a graphitic structure with distinctly marked two-dimensional crystalline order. They originate from the cathode material and are ejected in the form of glowing fragments directly from the cathode spot region. Consequently, their structure is comparable to that of extremely high heat-treated graphite¹⁸ and is expected to be fully degassed when impinging on the substrate. At exposure to air, however, a strong tendency to adsorption, similar to that of fine-grained graphite,²⁵ is probable. This assumption is proved by the mass density of the graphitic particles, which is (Rother-JMR, 108)</p> <p>distinctly lower than that of graphite (see Table IV). It should be noted that the large density difference of 10 to 20% may not be manifested by the much smaller medium deviations of the (002) distance illustrated in Fig. 5.</p> <p>The matrix material of the carbon coatings is directly formed from carbon ions whose energy and flux density affect the atomic arrangement of the growing substance. Referring to the crystalline carbon modifications, energies of approximately 60 eV are necessary to form a diamond crystal from single atoms.²⁶ In accordance with that value the most diamond-like structure of our thin films was determined at substances deposited with -50 to -100 V bias volt age. The EELS plots of that matrix material arc comparable to the data published by Martin et al.¹ who applied a macroparticle separation to the arc deposition process. Additionally, from electron diffraction experiments of the matrix material of our thin films, a diamond-like atomic near order to a distance of about 7 Å around an arbitrarily chosen atom was computed. The main feature of that amorphous structure, thereby, is the first atomic distance which is very close to that of diamond (see Table IV). (Rother-JMR, 109)</p>
Claim 26	
The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å	Coatings of some 10 nm up to 2.5 µm have been deposited on the substrates listed in Table I. According to the aims of this investigation, various deposition parameters have been applied (Table II). It should be noted that the deposition of well-adherent

'086 Patent	Rother, et al., 6 J. Mater. Res. 101-11 (Jan. 1991) ("Rother-JMR")																					
to 8000 Å.	<p>coatings with a thickness of more than 0.5 μm required an increased bias voltage of usually -400 V during the first 20 s of the deposition cycle. After that time the required dc or dc/rf bias supply was adjusted. For that purpose, in the case of the dc/rf bias mode, the dc bias was set to -100 V and the rf power was increased subsequently until the dc substrate current was zero. The deposition of thin films in the nanometer range proceeded, however, by adjusting the required bias voltage and bias mode prior to opening of the shutter and keeping them constant during deposition. (Rother-JMR, 102).</p> <div><p>TABLE II. Parameters and purposes of deposition.</p><table><tr><th>$U_b(\text{dc})/\text{V}$</th><th>$U_b(\text{dc} + \text{rf})/\text{V}(\text{dc})$</th><th>$j_s/\text{mA cm}^{-2}$</th><th>$\dot{d}_f/\mu\text{m min}^{-1}$</th><th>$d_f/\mu\text{m}$</th><th>Substrate materials^a</th><th>Purpose of deposition</th></tr><tr><td>-50 to -400</td><td></td><td>4</td><td>0.08</td><td>0.01-0.05</td><td>Silicon wafer</td><td>Structure analysis of the films' transmission electron microscopy</td></tr><tr><td>-50 to -400</td><td>-100</td><td>4-5</td><td>0.08-0.1</td><td>0.05-2.5</td><td>Silicon wafer, hardened ball bearing steel, stainless steel, cemented carbide</td><td>Structural and mechanical characterization of the coatings</td></tr></table><p>^a For detailed specification, see Table I. ^b Films from degassed and nondegassed cathodes were deposited for the purpose of comparison. U_b Bias voltage. j_s Substrate current density. \dot{d}_f Growth rate of the films. d_f Film thickness.</p></div> <p>(Rother-JMR, Table II)</p>	$U_b(\text{dc})/\text{V}$	$U_b(\text{dc} + \text{rf})/\text{V}(\text{dc})$	$j_s/\text{mA cm}^{-2}$	$\dot{d}_f/\mu\text{m min}^{-1}$	$d_f/\mu\text{m}$	Substrate materials ^a	Purpose of deposition	-50 to -400		4	0.08	0.01-0.05	Silicon wafer	Structure analysis of the films' transmission electron microscopy	-50 to -400	-100	4-5	0.08-0.1	0.05-2.5	Silicon wafer, hardened ball bearing steel, stainless steel, cemented carbide	Structural and mechanical characterization of the coatings
$U_b(\text{dc})/\text{V}$	$U_b(\text{dc} + \text{rf})/\text{V}(\text{dc})$	$j_s/\text{mA cm}^{-2}$	$\dot{d}_f/\mu\text{m min}^{-1}$	$d_f/\mu\text{m}$	Substrate materials ^a	Purpose of deposition																
-50 to -400		4	0.08	0.01-0.05	Silicon wafer	Structure analysis of the films' transmission electron microscopy																
-50 to -400	-100	4-5	0.08-0.1	0.05-2.5	Silicon wafer, hardened ball bearing steel, stainless steel, cemented carbide	Structural and mechanical characterization of the coatings																
Claim 27																						
The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.	<p>Coatings of some 10 nm up to 2.5 μm have been deposited on the substrates listed in Table I. According to the aims of this investigation, various deposition parameters have been applied (Table II). It should be noted that the deposition of well-adherent coatings with a thickness of more than 0.5 μm required an increased bias voltage of usually -400 V during the first 20 s of the deposition cycle. After that time the required dc or dc/rf bias supply was adjusted. For that purpose, in the case of the dc/rf bias mode, the dc bias was set to -100 V and the rf power was increased subsequently until the dc substrate current was zero. The deposition of thin films in the nanometer range proceeded, however, by adjusting the required bias voltage and bias mode prior to opening of the shutter and keeping them constant during deposition. (Rother-JMR, 102).</p>																					

'086 Patent	Rother, et al., 6 J. Mater. Res. 101-11 (Jan. 1991) ("Rother-JMR")																					
	<div>TABLE II. Parameters and purposes of deposition.</div> <table><tr><th>$U_b(\text{dc})/\text{V}$</th><th>$U_b(\text{dc} + \text{rf})/\text{V}(\text{dc})$</th><th>$j_s/\text{mA cm}^{-2}$</th><th>$\dot{d}_f/\mu\text{m min}^{-1}$</th><th>$d_f/\mu\text{m}$</th><th>Substrate materials^a</th><th>Purpose of deposition</th></tr><tr><td>-50 to -400</td><td></td><td>4</td><td>0.08</td><td>0.01-0.05</td><td>Silicon wafer</td><td>Structure analysis of the films' transmission electron microscopy</td></tr><tr><td>-50 to -400</td><td>-100</td><td>4-5</td><td>0.08-0.1</td><td>0.05-2.5</td><td>Silicon wafer, hardened ball bearing steel, stainless steel, cemented carbide</td><td>Structural and mechanical characterization of the coatings</td></tr></table> <div>^a For detailed specification, see Table I. ^b Films from degassed and nondegassed cathodes were deposited for the purpose of comparison. U_b Bias voltage. j_s Substrate current density. \dot{d}_f Growth rate of the films. d_f Film thickness.</div> <div>Table II</div>	$U_b(\text{dc})/\text{V}$	$U_b(\text{dc} + \text{rf})/\text{V}(\text{dc})$	$j_s/\text{mA cm}^{-2}$	$\dot{d}_f/\mu\text{m min}^{-1}$	$d_f/\mu\text{m}$	Substrate materials ^a	Purpose of deposition	-50 to -400		4	0.08	0.01-0.05	Silicon wafer	Structure analysis of the films' transmission electron microscopy	-50 to -400	-100	4-5	0.08-0.1	0.05-2.5	Silicon wafer, hardened ball bearing steel, stainless steel, cemented carbide	Structural and mechanical characterization of the coatings
$U_b(\text{dc})/\text{V}$	$U_b(\text{dc} + \text{rf})/\text{V}(\text{dc})$	$j_s/\text{mA cm}^{-2}$	$\dot{d}_f/\mu\text{m min}^{-1}$	$d_f/\mu\text{m}$	Substrate materials ^a	Purpose of deposition																
-50 to -400		4	0.08	0.01-0.05	Silicon wafer	Structure analysis of the films' transmission electron microscopy																
-50 to -400	-100	4-5	0.08-0.1	0.05-2.5	Silicon wafer, hardened ball bearing steel, stainless steel, cemented carbide	Structural and mechanical characterization of the coatings																
Claim 28																						
The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.	<p>Carbon films deposited by a modified dc cathodic arc technique were characterized by several analytical methods. The coating consists of two constituents originating from process characteristics of the technique applied. Small fragments of graphite are embedded in a matrix material of an amorphous structure with diamond-like short range order. The coating exhibits friction and wear reducing properties. (Rother-JMR, abstract)</p> <p>CADT-deposited carbon coatings are reported to exhibit exceptional hardness and high electrical resistivity.^{1,7} The structure of carbon thin films deposited by dc CADT with particle separation is described in terms of a diamond-like short-range order of carbon atoms.^{1,8} (Rother-JMR, 101)</p> <p>The combination of graphitic and diamond-like carbon phases proves to be a suitable coating material for mechanically stressed elements. It may also be expected that the rough carbon surface is eligible for the surface finish of medical implants. (Rother-JMR, 110)</p> <p>2. Matrix material</p> <p>Matrix material of the CADT-deposited c-C coatings was analyzed in the form of thin film areas by electron transmission techniques. In the course of the investigation of the films a separation of the matrix constituent could be achieved by careful adjustment of the areas under investigation.</p>																					

'086 Patent	Rother, et al., 6 J. Mater. Res. 101-11 (Jan. 1991) ("Rother-JMR")
	<p>ED experiments proved the amorphous structure of the c-C matrix material. Notwithstanding varying deposition parameters, the Diff(r) function computed from our ED data shows relatively sharp oscillations up to $r \approx 7 \text{ \AA}$, which indicates a near order extending over regions up to 14 \AA in diameter. Matrix materials of films deposited at bias voltages between -50 and (Rother-JMR, 105)</p> <p>-100 V, however, exhibit the most diamond-like structure and will be considered in the present paper in more detail. Table IV shows interatomic distances, coordination numbers, and mass density values obtained for our c-C matrix material in comparison with other carbon modifications. Figure 6 is a typical Diff(r) function of matrix material deposited at -100 V bias voltage. The first distinctly marked interatomic distance $r_1 = 1.51 \pm 0.05 \text{ \AA}$ corresponds closely to the value given for sp^3 bonds. The next maximum at $r_2 = 2.46 \pm 0.05 \text{ \AA}$ characterizes the second coordination sphere of carbon atoms being of a lower value than in crystalline diamond. (Rother-JMR, 106)</p> <p>Carbon coatings deposited by the dc cathodic arc technique consist of two substantially different constituents. The analysis of these two substances shows correspondence to data given in the literature and to well-established ideas of the film growth from free atoms and particles.</p> <p>In particular, the macroscopic particles in the coatings were determined to be of a graphitic structure with distinctly marked two-dimensional crystalline order. They originate from the cathode material and are ejected in the form of glowing fragments directly from the cathode spot region. Consequently, their structure is comparable to that of extremely high heat-treated graphite¹⁸ and is expected to be fully degassed when impinging on the substrate. At exposure to air, however, a strong tendency to adsorption, similar to that of fine-grained graphite,²⁵ is probable. This assumption is proved by the mass density of the graphitic particles, which is (Rother-JMR, 108)</p> <p>distinctly lower than that of graphite (see Table IV). It should be noted that the large density difference of 10 to 20% may not be manifested by the much smaller medium deviations of the (002) distance illustrated in Fig. 5.</p> <p>The matrix material of the carbon coatings is directly formed from</p>

'086 Patent	Rother, et al., 6 J. Mater. Res. 101-11 (Jan. 1991) ("Rother-JMR")
	<p>carbon ions whose energy and flux density affect the atomic arrangement of the growing substance. Referring to the crystalline carbon modifications, energies of approximately 60 eV are necessary to form a diamond crystal from single atoms.²⁶ In accordance with that value the most diamond-like structure of our thin films was determined at substances deposited with -50 to -100 V bias volt age. The EELS plots of that matrix material arc comparable to the data published by Martin et al.¹ who applied a macroparticle separation to the arc deposition process. Additionally, from electron diffraction experiments of the matrix material of our thin films, a diamond-like atomic near order to a distance of about 7 Å around an arbitrarily chosen atom was computed. The main feature of that amorphous structure, thereby, is the first atomic distance which is very close to that of diamond (see Table IV).</p> <p>(Rother-JMR, 109)</p>

'086 Patent	U.S. Patent No. 4,647,494 ("494 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The '494 patent issued Mar. 3, 1987. This is greater than one year before the '086 patent was filed on Jun. 14, 1994.</p> <p>Elements below show hard-carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>Improved wear-resistant coatings are provided for metallic magnetic recording layers, where the protective layer is comprised of hard carbon which adheres very well to the metallic magnetic layer. To ensure adherence between the hard carbon protective layer and the metallic magnetic layer, an interface layer of silicon is used. The silicon layer adheres very well to the underlying metallic magnetic layer, and can form metal silicides with this magnetic layer. The hard carbon layer adheres wel to the silicon layer, and forms an interfacial layer of silicon-carbon bonds. It is not the intent of this invention to form a silicon carbide layer (which is known as a wear-resistant material), but rather to provide a hard carbon layer having good adhesion to the magnetic substrate, due to the silicon layer. ('494 patent at 2:66-3:12).</p> <p>The specific compositions used for the substrate 12 and the metallic magnetic recording layer 14 can be varied, and include the types of materials generally known for these uses. For example, when hard magnetic recording disks are to be formed, the substrate 12 is typically glass, polymers, epoxies, ceramics, aluminum, or silicon. The metallic magnetic layer 14 is comprised of a thin film of a magnetic material or alloy, such as GdCo, CoPtCr, and CrV-CoPtCr, etc. The nature of the substrate 12 and the metallic magnetic recording layer 14 is not critical to the invention, and other materials can be used as long as the magnetic recording layer 14 is comprised of a metallic film. ('494 patent at 4:7-19).</p> <p>8. The recording medium of claim 1, where said substrate is selected from the group consisting of Al, Si, ceramics, epoxies, glass, and polymers. ('494 patent at 8:48-50).</p> <p>12. The recording medium of claim 10, where said substrate is selected from the group consisting of Al, Si, epoxies, ceramics, paper, glass, and polymers. ('494 patent at 9:3-5).</p> <p>17. The method of claim 16, where said substrate is selected from the</p>

'086 Patent	U.S. Patent No. 4,647,494 ("494 Patent")
	<p>group consisting of Al, Si, epoxies, ¹⁵ paper, glass, polymers, and ceramics. (⁴⁹⁴ patent at 10:13-15).</p>
<p>an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and</p>	<p>Generally, the silicon layer is about a monolayer-500 angstroms in thickness. It is only important that, after the silicon bonds to the metallic metal layer, that a continuous layer of silicon be available for bonding to the overlying hard carbon layer. Only a monolayer of continuous silicon is required for this purpose, as silicon and carbon can form Si-C bonds at room temperature. Thus, the silicon layer can be extremely thin and still provide strong adhesion to both the underlying metallic layer and the overlying hard carbon protective layer. This means that the recording head can be extremely close to the metallic magnetic recording layer, as is required in high density magnetic recording systems.</p> <p>The composite protective layer is comprised of silicon-Si/C bonds/hard carbon, although it is feasible to have all of the silicon used in the formation of silicides with the underlying metallic magnetic layer and Si/C bonds with the overlying hard carbon layer. (⁴⁹⁴ patent at 3:13-30).</p> <p>In the practice of this invention, hard carbon layers 18 are used as protective coatings over the metallic magnetic layer 14, and are made strongly adherent to the recording layer 14 by the use of an intermediate layer 16. This intermediate layer is silicon, which will form strong bonds with the underlying metallic magnetic layer 14 and with the overlying hard carbon layer 16. Silicon layer 16 serves as a nucleation layer, and its thickness is only such that a good bond will be formed to the underlying metallic layer 14 while leaving a continuous film of silicon for bonding to the overlying hard carbon layer 18. For the purpose of bonding to the hard carbon layer 18, only a few monolayers (that is, a layer a few atoms thick) is required, as long as the thin silicon layer is continuous. When the carbon layer 18 is thereafter deposited, very strong Si-C bonds will result, and silicon carbides may form at the interface 22 between the silicon layer 16 and the carbon layer 18. Similarly, the interface 24 between silicon layer 16 and the metallic magnetic layer 14 may be comprised of metal silicides, such as PtSi and CrSi, where the phase of the metal silicide that is formed depends upon the deposition temperature (substrate temperature). For example, Pt silicide can form at 280° C., while Cr silicides can form at 500° C. (⁴⁹⁴ patent at 4:20-44).</p> <p>It has been noted that the thickness of the deposited silicon layer 16 is not critical, as this layer is used as nucleation, or interface, layer.</p>

'086 Patent	U.S. Patent No. 4,647,494 ("494 Patent")
	<p>Typically, silicon is deposited to a thickness of about 10-50 angstroms, although a possible range is from a monolayer to about 500 angstroms.</p> <p>If silicon layer 16 is too thick, the recording density of the metallic magnetic layer 14 has to be decreased to ensure that write and read operations can be adequately performed. This is opposite to the desired direction of the technology and therefore is unacceptable. However, it will be understood that the principle of the present invention-the provision of a strongly adherent and very protective layer-will still be present even though the thickness of the silicon layer is more than the required minimum. In the circumstance of an overly thick silicon layer, the lower 20 angstroms or so of the silicon layer will strongly bond to the underlying metallic magnetic layer, while the upper-most 20 angstroms so of the silicon layer will form Si-C bonds with the overlying carbon layer 18. ('494 patent at 5:3-23).</p> <p>Prior to carbon deposition, the silicon substrates were etched for 30 seconds in a 10% HF solution for removal of any surface oxide layer. The hydros substrates were then exposed for 45 minutes to a hydrogen plasma in order to provide both reactive and sputtered cleaning of the growth surface and also a further hydroreduction of the native oxide layer on the silicon substrates. ('494 patent at 5:58-65).</p> <p>Further tests have indicated that a deposited silicon layer 16 of only a few atomic layers is able to provide extremely good adhesion of the hard carbon film 18 to the surface of the metallic layer 14. Adhesion tests indicate better adhesion to silicon layers of only a few atomic layers thickness as contrasted to that with thicker silicon intermediate layers. In order to deposit an amorphous silicon layer only a few angstroms thick as an intermediate adhesion layer, the silane plasma was applied for approximately 5-10 second, prior to the deposition of the carbon film 18. The main reason for the change in adhesion when thick silicon intermediate layers are used is most probably due to the formation of a larger amount of silicides between the deposited silicon layer and the underlying metallic magnetic layer. ('494 patent at 7:47-61).</p>
a hard carbon film arranged on said intermediate layer.	<p>As was noted, the hard carbon layer 18 is preferably deposited by plasma decomposition of a gas mixture, since this can be accomplished in the same vacuum system as the plasma deposition of silicon layer 16. However, a hard carbon layer can be deposited by other methods, such as sputtering. The thickness of the hard carbon</p>

'086 Patent	U.S. Patent No. 4,647,494 ("494 Patent")
	<p>layer 18 is usually about 250 angstroms, although its thickness can range from about 25 angstroms to about 1 micron. If the hard carbon film 18 has a thickness in excess of about 1 micron, adverse stresses usually develop. Further, in order to provide high recording density, it is desirable to keep the carbon layer 18 as thin as possible while still retaining the necessary wear-resistant qualities: atomic smoothness, ease of fabrication, and reproducibility. Carbon film 18 is an amorphous film which must be continuous in order to provide the necessary protective properties. (494 patent at 5:24-40).</p> <p>A superior wear-resistant coating is provided for metallic magnetic recording layers, where the improved coating is a hard carbon layer that is strongly bound to the underlying metallic magnetic recording layer by an intermediate layer of silicon. The silicon layer can be very thin, with a minimum thickness of a few atomic layers, and provides strong adhesion between the hard carbon protective layer and the metallic magnetic recording layer. A preferred technique for depositing both the intermediate silicon layer and the hard carbon layer is plasma deposition, since both of these depositions can be performed in the same reactor without breaking vacuum. (494 patent at Abstract).</p> <p>Improved wear-resistant coatings are provided for metallic magnetic recording layers, where the protective layer is comprised of hard carbon which adheres very well to the metallic magnetic layer. To ensure adherence between the hard carbon protective layer and the metallic magnetic layer, an interface layer of silicon is used. The silicon layer adheres very well to the underlying metallic magnetic layer, and can form metal silicides with this magnetic layer. The hard carbon layer adheres well to the silicon layer, and forms an interfacial layer of silicon-carbon bonds. It is not the intent of this invention to form a silicon carbide layer (which is known as a wear-resistant material), but rather to provide a hard carbon layer having good adhesion to the magnetic substrate, due to the silicon layer.(494 patent at 2:66-3:12).</p> <p>The composite protective layer is comprised of silicon-Si/C bonds/hard carbon, although it is feasible to have all of the silicon used in the formation of silicides with the underlying metallic magnetic layer and Si/C bonds with the overlying hard carbon layer. (494 patent at 3:26-30).</p> <p>Although hard carbon films are known as protective layers (K. Enke,</p>

'086 Patent	U.S. Patent No. 4,647,494 ("494 Patent")
	<p>Thin Solid Films, 80, p. 227, 1981), these carbon films will not adhere to metallic magnetic recording layers. However, in the practice of this invention, it has been discovered that hard carbon layers which are themselves very desirable for their mechanical properties can be used as protective layers for metallic magnetic recording if an intermediate layer of silicon is used to provide the necessary adhesion between the underlying magnetic recording layer and the overlying hard carbon protective layer. ('494 patent at 3:34-44).</p> <p>The hard carbon layer 18 and the interfacial layer 16 provide a strongly-adherent, wear-resistant coating without unduly increasing the separation between the recording head 20 and the metallic magnetic recording layer 14. ('494 patent at 4:2-6).</p> <p>In the practice of this invention, hard carbon layers 18 are used as protective coatings over the metallic magnetic layer 14, and are made strongly adherent to the recording layer 14 by the use of an intermediate layer 16. ('494 patent at 4:20-24).</p>
Claim 26	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p>Generally, the silicon layer is about a monolayer-500 angstroms in thickness. It is only important that, after the silicon bonds to the metallic metal layer, that a continuous layer of silicon be available for bonding to the overlying hard carbon layer. Only a monolayer of continuous silicon is required for this purpose, as silicon and carbon can form Si-C bonds at room temperature. ('494 patent at 3:13-19).</p> <p>It has been noted that the thickness of the deposited silicon layer 16 is not critical, as this layer is used as a nucleation, or interface, layer. Typically, silicon is deposited to a thickness of about 10-50 angstroms, although a possible range is from a monolayer to about 500 angstroms.</p> <p>If silicon layer 16 is too thick, the recording density of the metallic magnetic layer 14 has to be decreased to ensure that write and read operations can be adequately performed. This is opposite to the desired direction of the technology and therefore is unacceptable. However, it will be understood that the principle of the present invention-the provision of a strongly adherent and very protective layer-will still be present even though the thickness of the silicon layer is more than the required minimum. In the circumstance of an</p>

'086 Patent	U.S. Patent No. 4,647,494 ("494 Patent")
	<p>overly thick silicon layer, the lower 20 angstroms or so of the silicon layer will strongly bond to the underlying metallic magnetic layer, while the upper-most 20 angstroms or so of the silicon layer will form Si-C bonds with the overlying carbon layer 18.</p> <p>As was noted, the hard carbon layer 18 is preferably deposited by plasma decomposition of a gas mixture, since this can be accomplished in the same vacuum system as the plasma deposition of silicon layer 16. However, a hard carbon layer can be deposited by other methods, such as sputtering. The thickness of the hard carbon layer 18 is usually about 250 angstroms, although its thickness can range from about 25 angstroms to about 1 micron. ('494 patent at 5:3-32).</p> <p>In one test, a 400 angstrom thick hard carbon layer 18 was deposited onto an amorphous silicon layer of about 50 angstroms thickness. ('494 patent at 7:38-41).</p> <p>a protective coating for said metallic magnetic layer including a first continuous layer comprised of silicon deposited on said metallic magnetic recording layer, said silicon layer being deposited to a thickness less than 500 angstroms, and a nongraphitic hard carbon layer deposited on said silicon layer, said carbon layer having a thickness of about 25 angstroms-1 micron. ('494 patent at 8:22-29).</p> <p>a protective coating for said metallic magnetic layer comprising amorphous continuous silicon plasma-deposited on said metallic magnetic layer to a thickness less than 500 angstroms and nongraphitic amorphous hard carbon plasma-deposited on said amorphous silicon, said hard carbon having a thickness less than about 1 micron. ('494 patent at 8:59-65).</p> <p>depositing a continuous layer of silicon to a depth less than about 100 angstroms on said metallic magnetic recording layer by plasma deposition in a reactor, said plasma deposition decomposing a gas including a gas source of silicon, and plasma depositing a layer of nongraphitic hard carbon to a thickness less than about one micron on said deposited silicon layer, said plasma deposition of carbon occurring in said reactor by the introduction of a gaseous species including carbon into said reactor while maintaining substantially the same vacuum level in said reactor.</p> <p>16. The method of claim 15, where said silicon is deposited at amorphous silicon to a depth of at least a few atomic layers, and said</p>

'086 Patent	U.S. Patent No. 4,647,494 ("494 Patent")
	carbon is deposited as amorphous carbon to a thickness of at least about 25 angstroms. (494 patent at 9:19-10:12).
<u>Claim 27</u>	
The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.	<p>Generally, the silicon layer is about a monolayer-500 angstroms in thickness. It is only important that, after the silicon bonds to the metallic metal layer, that a continuous layer of silicon be available for bonding to the overlying hard carbon layer. Only a monolayer of continuous silicon is required for this purpose, as silicon and carbon can form Si-C bonds at room temperature. (494 patent at 3:13-19).</p> <p>It has been noted that the thickness of the deposited silicon layer 16 is not critical, as this layer is used as a nucleation, or interface, layer. Typically, silicon is deposited to a thickness of about 10-50 angstroms, although a possible range is from a monolayer to about 500 angstroms.</p> <p>If silicon layer 16 is too thick, the recording density of the metallic magnetic layer 14 has to be decreased to ensure that write and read operations can be adequately performed. This is opposite to the desired direction of the technology and therefore is unacceptable. However, it will be understood that the principle of the present invention-the provision of a strongly adherent and very protective layer-will still be present even though the thickness of the silicon layer is more than the required minimum. In the circumstance of an overly thick silicon layer, the lower 20 angstroms or so of the silicon layer will strongly bond to the underlying metallic magnetic layer, while the upper-most 20 angstroms or so of the silicon layer will form Si-C bonds with the overlying carbon layer 18.</p> <p>As was noted, the hard carbon layer 18 is preferably deposited by plasma decomposition of a gas mixture, since this can be accomplished in the same vacuum system as the plasma deposition of silicon layer 16. However, a hard carbon layer can be deposited by other methods, such as sputtering. The thickness of the hard carbon layer 18 is usually about 250 angstroms, although its thickness can range from about 25 angstroms to about 1 micron. (494 patent at 5:3-32).</p> <p>In one test, a 400 angstrom thick hard carbon layer 18 was deposited onto an amorphous silicon layer of about 50 angstroms thickness. (494 patent at 7:38-41).</p> <p>a protective coating for said metallic magnetic layer including a first</p>

'086 Patent	U.S. Patent No. 4,647,494 ("494 Patent")
	<p>continuous layer comprised of silicon deposited on said metallic magnetic recording layer, said silicon layer being deposited to a thickness less than 500 angstroms, and a nongraphitic hard carbon layer deposited on said silicon layer, said carbon layer having a thickness of about 25 angstroms-1 micron. ('494 patent at 8:22-29).</p> <p>a protective coating for said metallic magnetic layer comprising amorphous continuous silicon plasma-deposited on said metallic magnetic layer to a thickness less than 500 angstroms and nongraphitic amorphous hard carbon plasma-deposited on said amorphous silicon, said hard carbon having a thickness less than about 1 micron. ('494 patent at 8:59-65).</p> <p>depositing a continuous layer of silicon to a depth less than about 100 angstroms on said metallic magnetic recording layer by plasma deposition in a reactor, said plasma deposition decomposing a gas including a gas source of silicon, and plasma depositing a layer of nongraphitic hard carbon to a thickness less than about one micron on said deposited silicon layer, said plasma deposition of carbon occurring in said reactor by the introduction of a gaseous species including carbon into said reactor while maintaining substantially the same vacuum level in said reactor.</p> <p>16. The method of claim 15, where said silicon is deposited at amorphous silicon to a depth of at least a few atomic layers, and said carbon is deposited as amorphous carbon to a thickness of at least about 25 angstroms. ('494 patent at 9:19-10:7).</p>
<u>Claim 28</u>	
The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.	"Diamond-like carbon," is inherent based on the method of production.

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The '384 patent was filed on Jun. 24, 1985 and issued Nov. 17, 1987. This is greater than one year before the '086 patent was filed on Jun. 14, 1994.</p> <p>Elements below show hard-carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>A chemical vapor deposition method for the production of a composite body with one or more polycrystalline diamond layers, essentially free of intercrystalline binder phase, on a substrate of one of: (a) metalbonded hardmaterial compound; (b) ceramic material; or (c) a metal or an alloy, whereby the heated substrate is contacted with a gaseous mixture of hydrocarbon or hydrogen, which mixture has been activated by passing it over a tantalum heater heated to a temperature of 1500°-2500° C. ('384 patent at Abstract).</p> <p>Substrates or cores onto which reactively deposited diamond layers have been applied are numerous and include for instance metals such as Mo, W, Cu, Au, Nb, Ta, Ti, Co and an alloy such as W-Co, semiconductors such as Si, diamond itself and insulators such as glassy SiO₂. The following references provide an illustration of the state of the art: ('384 patent at 1:39-46).</p> <p>The core materials can also be made of alloys of other metals than precious metals, i.e. of any two or more common metals, possibly including precious metals, providing alloys stable in air under ordinary conditions and up to about 600° C. The preferred metals for such alloys are those of columns 1b to 7b and 8 of the periodical table of elements and include for instance copper, aluminium, silicon, titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, and the like. ('384 patent at 3:2-11).</p> <p>In some preferred embodiments, the coating material is selected from or contains metals, which are capable of forming stable carbides, for instance metals of columns 4b to 6b of the periodical table, preferably Ti. These may be applied in pure form as very thin layers or in combination with other metals which are capable of dissolving such metals and forming alloys. Metals having a high affinity to diamond because of their easy carbide formation property, ensure that the diamond layer adheres extremely well to the substrate by means of this intermediate layer, which acts as a binding layer.</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p>('384 patent at 3:31-41).</p> <p>1. A chemical vapour deposition (CVD) method for manufacturing a diamond clad composite body by depositing one or, successively, further adherent polycrystalline diamond layers substantially free from intercrystalline binder on (I) a core substrate selected from (a) metal bonded hard metallic compounds, (b) ceramic materials and (c) metals or alloys, said method involving contacting the heated core with an activated gaseous mixture of hydrocarbon and hydrogen, characterized in that said mixture is activated by passing over a tantalum heater to a temperature of 1500· to 2500· C. ('384 patent at 7:24-30).</p> <p>2. The method of claim 1 in which an intermediate layer IIB of a material selected from the group consisting of metals, ceramics and mixtures thereof is interposed between at least one of the core and the diamond layer and between the further diamond layers for improving physical and chemical properties. ('384 patent at 7:35-40).</p> <p>4. The method of claim 1 wherein the core material (Ib) is selected from borides, carbides, nitrides, and oxides of elements of columns 3a to 4a and 4b to 6b of the periodical table of elements and mixtures, solid solutions and compounds thereof. ('384 patent at 8:1-5).</p> <p>6. The method of claim 1, wherein the alloy material (Ic) of the core is selected from the solid mixtures of at least two metals of columns 3a to 4a, 1b to 7b and 8 of the periodical table of the elements. ('384 patent at 8:9-12).</p>
<p>an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and</p>	<p>The hydrocarbon is dissociated to reactive carbon which deposits on substrate 13. In the presence of hydrogen activated on the tantalum heater, this carbon deposited as well formed polycrystalline diamond layer 0.1 to several microns thick. ('384 patent at 4:46-50).</p> <p>Under the above-mentioned operating conditions, especially depending upon the heater temperature, the diamond layer mayor may not contain minute quantities of tantalum as intercrystalline inclusions. ('384 patent at 4:63-66).</p> <p>The chemical vapour deposition method permits to incorporate</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p>various dopants or inclusions within the diamond by using additives in the gaseous mixture. For instance, adding small amounts of diborane to the gas mixture produces boron-doped semi-conducting diamond layers. Or, by adding borazine in about 0.003% to 0.03% (v:v) to the hydrogen/hydrocarbon gaseous mixture, the polycrystalline diamond layer will include boron nitride co-deposited therein. This BN can consist of intercrystalline inclusions or be in solid solutions with the diamond. The presence of the BN will further improve some properties of the diamond containing laminated coatings of the present body.</p> <p>On the other hand, it is possible to prepare diamond layers which are substantially free from impurities by using very clean gases. In this way diamonds with extremely low nitrogen content can be obtained. These have a very high thermal conductivity and in this respect, they resemble the natural type 2A diamonds.</p> <p>Each individual layer of the cladding obtained from the method of the invention can be about 0.01 to about 10 μm thick, a range of 0.2 to 2 μm being preferred. However, when the cladding comprises more than one layer, its total thickness can reach 500 μm or more depending on the thickness of each layer and the number of layers. The number of layers can be two or many more and include several layers of diamond separated by non-diamond layers. The number of layers can be ten or more if desired, this number not being critical will depend on the specific applications.</p> <p>The method for depositing the non-diamond layers are standard methods well known from men skilled in the art and need not be described in many details here. All information on this aspect of the present work can be found in the following references: EP-A-83043 (METALLWERK PLANSEE); GB-A-1,425,633 (CUTANIT); US-A-3,837,896; US-A-4,284,687; GB-A-2,048,960; J. P. Chubb et al., Metals Technology, July (1980), p. 293-299. ('384 patent at 4:67-5:37).</p> <p>A cutting tool insert (substrate) made of cemented carbide was precoated with a layer of TiC 6 μm thick by CVD. ('384 patent at 5:56-58).</p> <p>A cemented carbide tool inserted in coated with a first 2 μm layer of TiC using a known CVD technique. ('384 patent at 6:25-26).</p> <p>The first layer of this coating is 0.5 μm of TiN deposited as in the previous examples, then the second layer is 2 μm of polycrystalline diamond also deposited as in the previous examples.</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p>The first two layers are followed by alternating 0.5 μm TiN and 2 μm diamond layers, the total being seven of each. (384 patent at 6:54-60).</p> <p>1. A chemical vapour deposition (CVD) method for manufacturing a diamond clad composite body by depositing one or, successively, further adherent polycrystalline diamond layers substantially free from intercrystalline binder on (I) a core substrate selected from (a) metal bonded hard metallic compounds, (b) ceramic materials and (c) metals or alloys, said method involving contacting the heated core with an activated gaseous mixture of hydrocarbon and hydrogen, characterized in that said mixture is activated by passing over a tantalum heater to a temperature of 1500° to 2500° C. (384 patent at 7:24-34).</p> <p>7. The method of claim 2, wherein the material of the intermediate layers (IIb) is selected from borides, carbides, nitrides and oxides of elements of columns 3a to 4a and 4b to 6b of the periodical table of elements and mixtures, solid solutions or compounds thereof. (384 patent at 8:13-17).</p> <p>9. The method of claim 1, wherein the material of the intermediate layers, although different from that of the core material, is selected from stable carbide forming metals or alloys containing such metals. (384 patent at 8:22-25).</p>
a hard carbon film arranged on said intermediate layer.	<p>The present invention concerns a chemical vapour deposition (CVD) method for manufacturing a diamond clad composite body by reactively depositing one or, successively, more adherent polycrystalline diamond layers substantially free from intercrystalline binders on (I) a core substrate selected from (a) metal bonded hard metallic compounds, (b) ceramic materials and (c) metals or alloys, said method involving contacting the heated core with an activated gaseous mixture of hydro-carbons and hydrogen. By the term of "reactively deposited diamond", one means diamond resulting from the thermal decomposition of carbon compounds, preferably hydrocarbons, into diamondgenerating carbon atoms preferentially from the gas phase activated in such a way as to avoid substantially the deposition of graphite carbon, said diamonds being deposited onto the substrates in the form of adherent individual crystallites or layer-like agglomerates of crystallites substantially free from intercrystalline adhesion binders. Adhesion binders are normally used for building sintered diamond powder layers, a material excluded from the present invention.</p> <p>Diamond layers of the aforementioned type are known and many</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p>deposition methods have been reported including chemical vapour deposition (CVD), for instance, the use of mixtures of hydrocarbons and hydrogen, said mixtures being activated for diamond deposition by passing over a hot thermionic emitter material such as a tungsten filament. ('384 patent at 1:7-36).</p> <p>When the object of the invention is to prepare composites having at least two layers in the cladding one of these being diamond and the other one consisting of a non-diamond material being interposed between the substrate core and the diamond layer, the purpose of the latter is to act as a binder layer to improve the adhesion of the diamond on the substrate or to improve other important properties like wear resistance or chemical resistance of the coated body. ('384 patent at 3:22-30).</p> <p>Metals having a high affinity to diamond because of their easy carbide formation property, ensure that the diamond layer adheres extremely well to the substrate by means of this intermediate layer, which acts as a binding layer. ('384 patent at 3:37-41).</p> <p>The object of the invention can be implemented by depositing on a selected core (I) one layer of CVD diamond or a combination of layers of non-diamond materials and CVD diamond, when the cladding comprises more than one layer, the order in which these layers are deposited is any; it may be chosen to achieve the desired properties, as will be illustrated in the different examples. ('384 patent at 3:42-49).</p> <p>The deposition of diamond in mineral substrates by the reaction of thermally decomposed hydrocarbons in the presence of hydrogen activated to the atomic state has been reported; (see for instance B. V. Spitsyn et al., J. of Crystal Growth 52, 219-26; S. Matsumoto et al., JP Kokai 58-91100). In the last of these references, a mixture of hydrocarbon and hydrogen is preheated by passing over a tungsten filament electrically heated to above 1000° C. and said preheated mixture is directed to the surface of a mineral substrate from 500° to 1300° C., whereby diamonds deposit in crystalline layer form on the surface of the substrate. ('384 patent at 3:57-68).</p> <p>The operating conditions suitable for obtaining diamond layers of the desired properties will now be disclosed with reference to the</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p>annexed drawing.</p> <p>FIG. 1 which represents a CVD apparatus for depositing diamonds on substrates.</p> <p>FIG. 2 represents the diamonds obtained according to the invention and</p> <p>FIG. 3 represents comparatively diamonds deposited by a prior art method (reference 10).</p> <p>('384 patent at 4:14-22).</p> <p>The hydrocarbon is dissociated to reactive carbon which deposits on substrate 13. In the presence of hydrogen activated on the tantalum heater, this carbon deposited as well formed polycrystalline diamond layer 0.1 to several microns thick.</p> <p>('384 patent at 4:47-50).</p> <p>This BN can consist of intercrystalline inclusions or be in solid solutions with the diamond. The presence of the BN will further improve some properties of the diamond containing laminated coatings of the present body. On the other hand, it is possible to prepare diamond layers which are substantially free from impurities by using very clean gases. In this way diamonds with extremely low nitrogen content can be obtained. These have a very high thermal conductivity and in this respect, they resemble the natural type 2A diamonds.</p> <p>Each individual layer of the cladding obtained from the method of the invention can be about 0.01 to about 10 μm thick, a range of 0.2 to 2 μm being preferred. However, when the cladding comprises more than one layer, its total thickness can reach 500 μm or more depending on the thickness of each layer and the number of layers. The number of layers can be two or many more and include several layers of diamond separated by non-diamond layers. The number of layers can be ten or more if desired, this number not being critical will depend on the specific applications.</p> <p>('384 patent at 5:7-28).</p> <p>The diamond layer is polycrystalline, composed of well shaped individual diamond crystals with smooth crystal faces and sharp edges, the grain size is about 1 to 3 μm (see FIG. 2).</p> <p>('384 patent at 6:4-7).</p> <p>Again a well shaped polycrystalline diamond deposit about 2 μm thick was obtained the performances of which in machining of cast iron and non-ferrous alloys is markedly improved with regard to an uncoated tool.</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p data-bbox="537 268 849 302">('384 patent at 6:19-22).</p> <p data-bbox="537 342 1414 485">After the first TiC layer is deposited, the insert is introduced into the apparatus disclosed with reference to FIG. 1 and it is further coated, under the conditions described in Example 1, with a layer of polycrystalline diamond 2 μm thick.</p> <p data-bbox="537 489 849 522">('384 patent at 6:27-31).</p> <p data-bbox="537 562 1425 743">A drilling bit is prepared by applying on the cutting tip of a cemented carbide drill a composite coating of hard materials. The first layer of this coating is 0.5 μm of TiN deposited as in the previous examples, then the second layer is 2 μm of polycrystalline diamond also deposited as in the previous examples.</p> <p data-bbox="537 747 849 781">('384 patent at 6:52-57).</p> <p data-bbox="537 821 1425 1001">A ceramic wear-part made of alumina for use as a wire drawing die is coated with a 2.5 μm layer of polycrystalline diamond according to the invention under the conditions of Example 1 except for the following parameters: substrate temperature 815°C.; gas flow 100 ml/min (standard conditions); duration 24 hours.</p> <p data-bbox="537 1005 849 1039">('384 patent at 6:67-7:5).</p> <p data-bbox="537 1079 1425 1180">After the first layer of alumina, the latter is further coated with diamond using the conditions of the previous examples; thickness 1.8 μm.</p> <p data-bbox="537 1184 849 1218">('384 patent at 7:10-12).</p> <p data-bbox="537 1257 1284 1291">A typical diamond like polycrystalline deposit is obtained.</p> <p data-bbox="537 1295 849 1329">('384 patent at 7:21-22).</p> <p data-bbox="537 1369 1393 1470">11. The method of claim 1, wherein the diamond further comprises boron, nitrogen or mixtures thereof as non binder intercrystalline inclusions or dopant materials in solid solution.</p> <p data-bbox="537 1474 1339 1545">12. The method of claim 1, wherein the nitrogen content of the diamond layer is below 100 ppm.</p> <p data-bbox="537 1549 1398 1650">13. The method of claim 1, wherein the diamond and intermediate layers have a thickness of 0.01 to 10 microns each and the cladding has a thickness of 0.1-500 microns.</p> <p data-bbox="537 1654 849 1688">('384 patent at 8:29-38).</p> <p data-bbox="537 1728 1425 1829">15. The method of claim 11, in which the diamond layer contains BN and comprises using borazine as a further components of the gaseous mixtures.</p> <p data-bbox="537 1833 849 1866">('384 patent at 8:41-43).</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
<u>Claim 26</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p>In the presence of hydrogen activated on the tantalum heater, this carbon deposited as well formed polycrystalline diamond layer 0.1 to several microns thick. ('384 patent at 4:47-50).</p> <p>Each individual layer of the cladding obtained from the method of the invention can be about 0.01 to about 10 μm thick, a range of 0.2 to 2 μm being preferred. However, when the cladding comprises more than one layer, its total thickness can reach 500 μm or more depending on the thickness of each layer and the number of layers. The number of layers can be two or many more and include several layers of diamond separated by non-diamond layers. The number of layers can be ten or more if desired, this number not being critical will depend on the specific applications. ('384 patent at 5:18-28).</p> <p>The average coating thickness was about 2 μm. ('384 patent at 6:2-3).</p> <p>Again a well shaped polycrystalline diamond deposit about 2 μm thick was obtained the performances of which in machining of cast iron and non-ferrous alloys is markedly improved with regard to an uncoated tool. ('384 patent at 6:19-22).</p> <p>After the first TiC layer is deposited, the insert is introduced into the apparatus disclosed with reference to FIG. 1 and it is further coated, under the conditions described in Example 1, with a layer of polycrystalline diamond 2 μm thick. ('384 patent at 6:27-31).</p> <p>Example 3 is repeated in all details with the following exception: after the first layer of TiC (2 μm) is deposited, an intermediate about 0.1 μm thick layer of pure titanium is placed over the TiC to provide improved adhesion toward the subsequent polycrystalline diamond layer. ('384 patent at 6:40-45).</p> <p>The first layer of this coating is 0.5 μm of TiN deposited as in the previous examples, then the second layer is 2 J.Lm of polycrystalline diamond also deposited as in the previous examples. The first two layers are followed by alternating 0.5 μm TiN and 2 μm</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p>diamond layers, the total being seven of each. The total thickness of the coating is 17.5 μm. ('384 patent at 6:54-60).</p> <p>A ceramic wear-part made of alumina for use as a wire drawing die is coated with a μm layer of polycrystalline diamond according to the invention. ('384 patent at 6:67-7:1).</p> <p>13. The method of claim 1, wherein the diamond and intermediate layers have a thickness of 0.01 to 10 microns each and the cladding has a thickness of 0.1-500 microns. ('384 patent at 8:35-38).</p>
<u>Claim 27</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.</p>	<p>The hydrocarbon is dissociated to reactive carbon which deposits on substrate 13. In the presence of hydrogen activated on the tantalum heater, this carbon deposited as well formed polycrystalline diamond layer 0.1 to several microns thick. ('384 patent at 4:47-50).</p> <p>Again a well shaped polycrystalline diamond deposit about 2 μm thick was obtained the performances of which in machining of cast iron and non-ferrous alloys is markedly improved with regard to an uncoated tool. ('384 patent at 6:19-22).</p> <p>After the first TiC layer is deposited, the insert is introduced into the apparatus disclosed with reference to FIG. 1 and it is further coated, under the conditions described in Example 1, with a layer of polycrystalline diamond 2 μm thick. ('384 patent at 6:27-31).</p> <p>Example 3 is repeated in all details with the following exception: after the first layer of TiC (2 μm) is deposited, an intermediate about 0.1 μm thick layer of pure titanium is placed over the TiC to provide improved adhesion toward the subsequent polycrystalline diamond layer. ('384 patent at 6:40-45).</p> <p>The first layer of this coating is 0.5 μm of TiN deposited as in the previous examples, then the second layer is 2 μm of polycrystalline diamond also deposited as in the previous examples.</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p>The first two layers are followed by alternating 0.5 μm TiN and 2 μm diamond layers, the total being seven of each. The total thickness of the coating is 17.5 μm. ('384 patent at 6:54-60).</p> <p>A ceramic wear-part made of alumina for use as a wire drawing die is coated with a μm layer of polycrystalline diamond according to the invention. ('384 patent at 6:67-7:1).</p> <p>13. The method of claim 1, wherein the diamond and intermediate layers have a thickness of 0.01 to 10 microns each and the cladding has a thickness of 0.1-500 microns. ('384 patent at 8:35-38).</p> <p>Each individual layer of the cladding obtained from the method of the invention can be about 0.01 to about 10 μm thick, a range of 0.2 to 2 μm being preferred. However, when the cladding comprises more than one layer, its total thickness can reach 500 μm or more depending on the thickness of each layer and the number of layers. The number of layers can be two or many more and include several layers of diamond separated by non-diamond layers. The number of layers can be ten or more if desired, this number not being critical will depend on the specific applications. ('384 patent at 5:18-28).</p> <p>The average coating thickness was about 2 μm. ('384 patent at 6:2-3).</p>
<u>Claim 28</u>	
<p>The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.</p>	<p>The present invention concerns a chemical vapour deposition (CVD) method for manufacturing a diamond clad composite body by reactively depositing one or, successively, more adherent polycrystalline diamond layers substantially free from intercrystalline binders on (I) a core substrate selected from (a) metal bonded hard metallic compounds, (b) ceramic materials and (c) metals or alloys, said method involving contacting the heated core with an activated gaseous mixture of hydro-carbons and hydrogen. By the term of "reactively deposited diamond", one means diamond resulting from the thermal decomposition of carbon compounds, preferably hydrocarbons, into diamond generating carbon atoms preferentially from the gas phase activated in such a way as to avoid substantially the deposition of graphite carbon, said diamonds being deposited onto the substrates in the form of adherent individual crystallites or layer-like agglomerates of crystallites substantially free from</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p>intercrystalline adhesion binders. Adhesion binders are normally used for building sintered diamond powder layers, a material excluded from the present invention.</p> <p>Diamond layers of the aforementioned type are known and many deposition methods have been reported including chemical vapour deposition (CVD), for instance, the use of mixtures of hydrocarbons and hydrogen, said mixtures being activated for diamond deposition by passing over a hot thermionic emitter material such as a tungsten filament. ('384 patent at 1:7-36).</p> <p>When the object of the invention is to prepare composites having at least two layers in the cladding one of these being diamond and the other one consisting of a non-diamond material being interposed between the substrate core and the diamond layer, the purpose of the latter is to act as a binder layer to improve the adhesion of the diamond on the substrate or to improve other important properties like wear resistance or chemical resistance of the coated body. ('384 patent at 3:22-30).</p> <p>Metals having a high affinity to diamond because of their easy carbide formation property, ensure that the diamond layer adheres extremely well to the substrate by means of this intermediate layer, which acts as a binding layer. ('384 patent at 3:37-41).</p> <p>The object of the invention can be implemented by depositing on a selected core (I) one layer of CVD diamond or a combination of layers of non-diamond materials and CVD diamond, when the cladding comprises more than one layer, the order in which these layers are deposited is any; it may be chosen to achieve the desired properties, as will be illustrated in the different examples. ('384 patent at 3:42-49).</p> <p>The deposition of diamond in mineral substrates by the reaction of thermally decomposed hydrocarbons in the presence of hydrogen activated to the atomic state has been reported; (see for instance B. V. Spitsyn et al., J. of Crystal Growth 52, 219-26; S. Matsumoto et al., JP Kokai 58-91100). In the last of these references, a mixture of hydrocarbon and hydrogen is preheated by passing over a tungsten filament electrically heated to above 1000° C. and said preheated mixture is directed to the surface of a mineral substrate from 500° to 1300° C., whereby diamonds deposit in crystalline layer form on the surface of the substrate.</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p data-bbox="537 268 850 302">('384 patent at 3:57-68).</p> <p data-bbox="537 342 1422 447">The operating conditions suitable for obtaining diamond layers of the desired properties will now be disclosed with reference to the annexed drawing.</p> <p data-bbox="537 453 1430 520">FIG. 1 which represents a CVD apparatus for depositing diamonds on substrates.</p> <p data-bbox="537 527 1398 594">FIG. 2 represents the diamonds obtained according to the invention and</p> <p data-bbox="537 600 1386 667">FIG. 3 represents comparatively diamonds deposited by a prior art method (reference 10).</p> <p data-bbox="537 674 850 707">('384 patent at 4:14-22).</p> <p data-bbox="537 747 1417 890">The hydrocarbon is dissociated to reactive carbon which deposits on substrate 13. In the presence of hydrogen activated on the tantalum heater, this carbon deposited as well formed polycrystalline diamond layer 0.1 to several microns thick.</p> <p data-bbox="537 896 850 930">('384 patent at 4:47-50).</p> <p data-bbox="537 970 1417 1289">This BN can consist of intercrystalline inclusions or be in solid solutions with the diamond. The presence of the BN will further improve some properties of the diamond containing laminated coatings of the present body. On the other hand, it is possible to prepare diamond layers which are substantially free from impurities by using very clean gases. In this way diamonds with extremely low nitrogen content can be obtained. These have a very high thermal conductivity and in this respect, they resemble the natural type 2A diamonds.</p> <p data-bbox="537 1295 1430 1619">Each individual layer of the cladding obtained from the method of the invention can be about 0.01 to about 10 μm thick, a range of 0.2 to 2 μm being preferred. However, when the cladding comprises more than one layer, its total thickness can reach 500 μm or more depending on the thickness of each layer and the number of layers. The number of layers can be two or many more and include several layers of diamond separated by non-diamond layers. The number of layers can be ten or more if desired, this number not being critical will depend on the specific applications.</p> <p data-bbox="537 1625 834 1659">('384 patent at 5:7-28).</p> <p data-bbox="537 1698 1357 1803">The diamond layer is polycrystalline, composed of well shaped individual diamond crystals with smooth crystal faces and sharp edges, the grain size is about 1 to 3 μm (see FIG. 2).</p> <p data-bbox="537 1810 818 1843">('384 patent at 6:4-7).</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	<p>Again a well shaped polycrystalline diamond deposit about 2 μm thick was obtained the performances of which in machining of cast iron and non-ferrous alloys is markedly improved with regard to an uncoated tool. ('384 patent at 6:19-22).</p> <p>After the first TiC layer is deposited, the insert is introduced into the apparatus disclosed with reference to FIG. 1 and it is further coated, under the conditions described in Example 1, with a layer of polycrystalline diamond 2 μm thick. ('384 patent at 6:27-31).</p> <p>A drilling bit is prepared by applying on the cutting tip of a cemented carbide drill a composite coating of hard materials. The first layer of this coating is 0.5 μm of TiN deposited as in the previous examples, then the second layer is 2 μm of polycrystalline diamond also deposited as in the previous examples. ('384 patent at 6:52-57).</p> <p>A ceramic wear-part made of alumina for use as a wire drawing die is coated with a 2.5 μm layer of polycrystalline diamond according to the invention under the conditions of Example 1 except for the following parameters: substrate temperature 815°C.; gas flow 100 ml/min (standard conditions); duration 24 hours. ('384 patent at 6:67-7:5).</p> <p>After the first layer of alumina, the latter is further coated with diamond using the conditions of the previous examples; thickness 1.8 μm. ('384 patent at 7:10-12).</p> <p>A typical diamond like polycrystalline deposit is obtained. ('384 patent at 7:21-22).</p> <p>11. The method of claim 1, wherein the diamond further comprises boron, nitrogen or mixtures thereof as non binder intercrystalline inclusions or dopant materials in solid solution.</p> <p>12. The method of claim 1, wherein the nitrogen content of the diamond layer is below 100 ppm.</p> <p>13. The method of claim 1, wherein the diamond and intermediate layers have a thickness of 0.01 to 10 microns each and the cladding has a thickness of 0.1-500 microns. ('384 patent at 8:29-38).</p>

'086 Patent	U.S. Patent No. 4,707,384 ("384 Patent")
	15. The method of claim 11, in which the diamond layer contains BN and comprises using borazine as a further components of the gaseous mixtures. (384 patent at 8:41-43).

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The '349 patent was filed on Apr. 11, 1994 and issued Jan. 10, 1995, and claiming priority back to Dec. 7, 1988. This is prior to filing of the '086 patent on Jun. 14, 1994.</p> <p>Elements below show hard-carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>This substrate should preferably be a material suitable for formation of diamond film, and at the same time a material which can be polished and etched, and also can finish its surface roughness to a mirror surface of 0.05 μm or less in terms of R_{max} by polishing. As such material, Si, W, Mo, Ta, SiC, WC, Si_3N_4, SiO_2, Al_2O_3, etc. may be included. ('349 patent at 6:15-21).</p>
an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and	<p>First, the substrate surface is mirror polished to a surface roughness, which is preferably 0.05 μm or less in terms of R_{max}, more preferably 0.01 μm or less. Next, diamond abrasive particles with an average particle size of 10 to 20 μm are dispersed in an alcohol, the above substrate is placed in this solution and then the solution is subjected to sonication vibration, thereby effecting fine damaging treatment on the substrate surface.</p> <p>During this operation, it is preferable to optimize the conditions for damaging treatment so that the surface roughness of the substrate surface may not exceed 0.05 μm in terms of R_{max}. Thereafter, a diamond thin film is formed to several μm to some 100 μm by the microwave plasma CVD method, the hot filament CVD method, the plasma jet method, the ECR plasma CVD method, etc. The gases employed at this time may be carbon containing gases, including hydrocarbons such as methane, ethane, propane, ethylene, benzene, acetylene, etc.; halogenated carbons such as methylene chloride, carbon tetrachloride, chloroform, trichloroethane, etc.; alcohols such as methyl alcohol, ethyl alcohol, etc.; ketones such as $(\text{CH}_3)_2$, $(\text{C}_6\text{H}_5)\text{CO}$, etc.; gases such as CO, CO_2, etc. and mixtures of these gases with gases such as N_2, H_2, O_2, H_2O, Ar, etc. ('349 patent at 6:22-46).</p> <p>Next, the surface of the diamond film formed bonded onto the mold surface of a material which can easily be precisely worked as the matrix of mold for press molding and has heat resistance and hot impact resistance, such as tungsten carbide, thermet, zirconia, etc. The bonding agent in this case may be preferably one which is good in wettability with diamond and can assure sufficient mechanical strength and geometrical dimensional precision under the conditions</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>(heating temperature, pressing pressure, etc.) of optical element molding. As such material, there may be included elements such as Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, AU, Si, Ge, Sn, Pb, etc., or compounds, mixtures of one kind or two or more kinds of these, or alloys such as Ag-Cu, Ag-Sn, Ti-Ag, Ti-Cu, Ti-Co, Ti-Ni, Au-Nb, Au-Ta, etc. ('349 patent at 6:47-64).</p> <p>Also, on the mold matrix to be bonded, a bonding agent layer for solid phase bonding is formed. The bonding agent may be preferably one which has good adhesion to the mold matrix and sufficient strength by bonding, and at the same time sufficient bonding strength under the conditions (heating temperature, pressing pressure, etc.) of optical element molding.</p> <p>Particularly, it is critical that it should have a thermal expansion coefficient approximate to the both. For example, when the mold matrix is made of tungsten carbide, Ti, Ta, Ni, etc. are suitable. In carrying out bonding, it is preferable to use the same kind of material for the film on the diamond film and the mm on the mold matrix and bond the diamond film onto the mold matrix by solid phase mutually bonding between the same kind of materials.</p> <p>The bonding agent in this case is formed by vacuum vapor deposition, sputtering, ion plating or plating. The film thickness of the bonding agent may be such that the unevenness of the surface of the diamond mm can be flattened on the diamond mm side, and adhesion is not lowered through internal stress of the film, namely generally within the range of 1 to 10 μm, preferably 2 to 4 μm. Also, the film thickness of the film on the mold matrix and the layer participating in solid phase bonding, namely the solid phase bonding layer may be equal to this. Next, for effecting solid phase bonding, pressing may be carried out in vacuum higher than 1×10^{-4} Torr, at a bonding temperature of 700° to 900° C. and pressure of 0.1 to 10 kg/cm^2. The press time in this case, which may differ on the plane precision of the bonding face, etc., may be about 30 minutes to 3 hours. The solid phase bonding is not necessarily effected mutually between the same kind of materials but different kinds of materials may be employed. However, in the latter case, the film thickness range from 100 μm to 1 mm, and the bonding temperature, the pressig pressure, the pressing time, etc. are higher or longer than the case of the same kind of materials. ('349 patent at 6:65-7:36).</p> <p>After the diamond film is bonded onto the mold matrix the substrate used for formation of the diamond film is removed by polishing or</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>etching. As a result, the diamond film can be formed as reversed on the mold matrix. Since the surface of the diamond film has the shape of the substrate surface transferred thereon, it is very smooth as different from the surface inherent in the diamond film, and its surface roughness can be made 0.05 μm or less in terms of R_{max}. However, when the mold shape is slipped from the desired shape by bonding or when the surface roughness exceeds 0.05 μm in terms of R_{max}, the shape and the surface roughness can be modified to desired ones by use of the polishing method of diamond single crystal generally known in the art. ('349 patent at 7:37-50).</p> <p>By means of the microwave plasma CVD device shown in FIG. 6, a diamond thin film is precipitated to 5 μm on a mold matrix comprising WC-10% Co. At this time, the surface of the mold matrix is subjected to the damaging treatment after the mirror surface working of the molding face shape in a sonication washer in a solution of diamond abrasive particles with a particle size of 15 μm dispersed in ethyl alcohol for one hour in order to enhance diamond nucleation density. Depending on the extent of mirror surface working, no damaging treatment as mentioned above may be performed. Formation of the diamond thin film is performed by means of the microwave plasma CVD device shown in FIG. 6 by first evacuating to 1×10^{-7} Torr by the evacuation system 201, and then delivering the gases from the gas feeding system 202 at the flow rates of $\text{CH}_4=2$ SCCM, $\text{H}_2=98$ SCCM to the reaction chamber to make the pressure in the reaction chamber 35 Torr. Next, by use of the microwave 203 of 2.45 GHz, a diamond polycrystalline film with a thickness of 5 μm is formed on the mold matrix with the power of the microwave being 400 W. At this time, the temperature of the mold matrix is made 850° C. The surface roughness of the diamond thin film obtained is measured by a contact needle type surface roughness meter to be 0.3 μm of R_{max}. It is also conformed by X-ray diffraction that the (100) face is oriented substantially in parallel to the substrate surface. ('349 patent at 14:3-30).</p> <p>By use of the mold matrix as described above, by means of the microwave plasma CVD device shown in FIG. 6, evacuation is effected similarly, and then through the gas feeding system 202, CH_4 is flowed at 0.5 SCCM and H_2 at 99.5 SCCM, to make the pressure in the reaction chamber 35 Torr, and a diamond thin film a thickness of about 5 μm is formed on the mold matrix by microwave discharging under the same conditions. At this time, the temperature</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>of the mold matrix is 850°C. The surface roughness of the film obtained is 1 µm in terms of Rmax. By X-ray diffraction, (111), (110) peaks are obtained, and particularly it is found to be a film composed mainly of the (111) face. Next, when the film surface is polished similarly as described above, the surface roughness of the film surface after polishing is 0.05 µm in terms of Rmax and the film thickness 3 µm. The polishing speed at this time is 0.4 µm/h. ('349 patent at 14:47-63).</p> <p>The mold for optical element molding shown in FIG. 9 comprises WC (90%) + Co (10%), and the molding face is mirror finished to 0.01 µm or less in terms of Rmax. The surface of the substrate 1 comprising Si fitted to the mold is polished similarly to Rmax<0.01 µm. Next, said substrate 1 is placed in a solution of diamond abrasive particles with an average particle size of 10 to 15 µm dispersed in ethyl alcohol, and damaging treatment is applied on its surface by sonication vibration for 1.5 hours. The surface roughness of this substrate is measured to be Rmax=0.10 µm. Next, by means of the microwave plasma CVD device shown in FIG. 6, first evacuation is effected to 1 X 10⁻⁷ Torr by the evacuation system 2, and then the gasses are delivered through the gas feeding system 3 into the reaction chamber at CH₄=0.8 SCCM and H₂=99.2 SCCM to make the pressure in the reaction chamber 40 Torr. Next, by use of the microwave 4 of 2.45 GHz with the power of microwave being made 450 W, a diamond polycrystalline film with a thickness of about 10 µm is formed on the Si substrate. At this time, the substrate temperature is made 850° C. The surface roughness of the diamond thin film obtained is measured by a contact needle type surface roughness meter to be 0.6 µm of Rmax. Here, with the diamond thin film of 1µm thickness formed under the same conditions, it is a polycrystalline film with an average particle size of 0.3 µm to 0.4 µm and a nucleation density of 6 to 9 µm⁻². Next, after Ti is formed to about 3 µm by sputtering on the diamond thin film, Ag is formed to about 3 µm according to vacuum vapor deposition. Similarly, after Ni is formed to about 3 µm on the mold surface by ion plating, Ag is formed to about 3µm by vacuum vapor deposition. After the substrate and the mold matrix are fitted together, heating is effected in vacuum at 850° C. to bond the substrate and the mold matrix. Here, bonding between the substrate and the mold matrix is effected by fixing under a uniform force of about 0.15 kg/mm² for about 3 hours. ('349 patent at 18:27-65).</p>
a hard carbon film	First, the substrate surface is mirror polished to a surface roughness,

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
arranged on said intermediate layer.	<p>which is preferably 0.05 μm or less in terms of R_{max}, more preferably 0.01 μm or less. Next, diamond abrasive particles with an average particle size of 10 to 20 μm are dispersed in an alcohol, the above substrate is placed in this solution and then the solution is subjected to sonication vibration, thereby effecting fine damaging treatment on the substrate surface.</p> <p>During this operation, it is preferable to optimize the conditions for damaging treatment so that the surface roughness of the substrate surface may not exceed 0.05 μm in terms of R_{max}. Thereafter, a diamond thin film is formed to several μm to some 100 μm by the microwave plasma CVD method, the hot filament CVD method, the plasma jet method, the ECR plasma CVD method, etc. The gases employed at this time may be carbon containing gases, including hydrocarbons such as methane, ethane, propane, ethylene, benzene, acetylene, etc.; halogenated carbons such as methylene chloride, carbon tetrachloride, chloroform, trichloroethane, etc.; alcohols such as methyl alcohol, ethyl alcohol, etc.; ketones such as $(\text{CH}_3)_2$, $(\text{C}_6\text{H}_5)\text{CO}$, etc.; gases such as CO, CO_2, etc. and mixtures of these gases with gases such as N_2, H_2, O_2, H_2O, Ar, etc. ('349 patent at 6:22-46).</p> <p>Next, the surface of the diamond film formed bonded onto the mold surface of a material which can easily be precisely worked as the matrix of mold for press molding and has heat resistance and hot impact resistance, such as tungsten carbide, thermet, zirconia, etc. The bonding agent in this case may be preferably one which is good in wettability with diamond and can assure sufficient mechanical strength and geometrical dimensional precision under the conditions (heating temperature, pressing pressure, etc.) of optical element molding. As such material, there may be included elements such as Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Si, Ge, Sn, Pb, etc., or compounds, mixtures of one kind or two or more kinds of these, or alloys such as Ag-Cu, Ag-Sn, Ti-Ag, Ti-Cu, Ti-Co, Ti-Ni, Au-Nb, Au-Ta, etc. ('349 patent at 6:47-64).</p> <p>Also, on the mold matrix to be bonded, a bonding agent layer for solid phase bonding is formed. The bonding agent may be preferably one which has good adhesion to the mold matrix and sufficient strength by bonding, and at the same time sufficient bonding strength under the conditions (heating temperature, pressing pressure, etc.) of optical element molding.</p> <p>Particularly, it is critical that it should have a thermal expansion coefficient approximate to the both. For example, when the mold</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>matrix is made of tungsten carbide, Ti, Ta, Ni, etc. are suitable. In carrying out bonding, it is preferable to use the same kind of material for the film on the diamond film and the mm on the mold matrix and bond the diamond film onto the mold matrix by solid phase mutually bonding between the same kind of materials.</p> <p>The bonding agent in this case is formed by vacuum vapor deposition, sputtering, ion plating or plating. The film thickness of the bonding agent may be such that the unevenness of the surface of the diamond mm can be flattened on the diamond mm side, and adhesion is not lowered through internal stress of the film, namely generally within the range of 1 to 10 μm, preferably 2 to 4 μm. Also, the film thickness of the film on the mold matrix and the layer participating in solid phase bonding, namely the solid phase bonding layer may be equal to this. Next, for effecting solid phase bonding, pressing may be carried out in vacuum higher than 1×10^{-4} Torr, at a bonding temperature of 700° to 900° C. and pressure of 0.1 to 10 kg/cm^2. The press time in this case, which may differ on the plane precision of the bonding face, etc., may be about 30 minutes to 3 hours. The solid phase bonding is not necessarily effected mutually between the same kind of materials but different kinds of materials may be employed. However, in the latter case, the film thickness range from 100 μm to 1 mm, and the bonding temperature, the press pressure, the pressing time, etc. are higher or longer than the case of the same kind of materials.</p> <p>('349 patent at 6:65-7:36).</p> <p>After the diamond film is bonded onto the mold matrix the substrate used for formation of the diamond film is removed by polishing or etching. As a result, the diamond film can be formed as reversed on the mold matrix. Since the surface of the diamond film has the shape of the substrate surface transferred thereon, it is very smooth as different from the surface inherent in the diamond film, and its surface roughness can be made 0.05 μm or less in terms of R_{max}. However, when the mold shape is slipped from the desired shape by bonding or when the surface roughness exceeds 0.05 μm in terms of R_{max}, the shape and the surface roughness can be modified to desired ones by use of the polishing method of diamond single crystal generally known in the art.</p> <p>('349 patent at 7:37-50).</p> <p>By means of the microwave plasma CVD device shown in FIG. 6, a diamond thin film is precipitated to 5 μm on a mold matrix comprising WC-10% Co. At this time, the surface of the mold matrix is subjected to the damaging treatment after the mirror surface</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>working of the molding face shape in a sonication washer in a solution of diamond abrasive particles with a particle size of 15 μm dispersed in ethyl alcohol for one hour in order to enhance diamond nucleation density. Depending on the extent of mirror surface working, no damaging treatment as mentioned above may be performed. Formation of the diamond thin film is performed by means of the microwave plasma CVD device shown in FIG. 6 by first evacuating to 1×10^{-7} Torr by the evacuation system 201, and then delivering the gases from the gas feeding system 202 at the flow rates of $\text{CH}_4=2$ SCCM, $\text{H}_2=98$ SCCM to the reaction chamber to make the pressure in the reaction chamber 35 Torr. Next, by use of the microwave 203 of 2.45 GHz, a diamond polycrystalline film with a thickness of 5 μm is formed on the mold matrix with the power of the microwave being 400 W. At this time, the temperature of the mold matrix is made 850° C. The surface roughness of the diamond thin film obtained is measured by a contact needle type surface roughness meter to be 0.3 μm of Rmax. It is also conformed by X-ray diffraction that the (100) face is oriented substantially in parallel to the substrate surface. (349 patent at 14:3-30).</p> <p>By use of the mold matrix as described above, by means of the microwave plasma CVD device shown in FIG. 6, evacuation is effected similarly, and then through the gas feeding system 202, CH_4 is flowed at 0.5 SCCM and H_2 at 99.5 SCCM, to make the pressure in the reaction chamber 35 Torr, and a diamond thin film a thickness of about 5 μm is formed on the mold matrix by microwave discharging under the same conditions. At this time, the temperature of the mold matrix is 850°C. The surface roughness of the film obtained is 1 μm in terms of Rmax. By X-ray diffraction, (111), (110) peaks are obtained, and particularly it is found to be a film composed mainly of the (111) face. Next, when the film surface is polished similarly as described above, the surface roughness of the film surface after polishing is 0.05 μm in terms of Rmax and the film thickness 3 μm. The polishing speed at this time is 0.4 $\mu\text{m}/\text{h}$. (349 patent at 14:47-63).</p> <p>The mold for optical element molding shown in FIG. 9 comprises WC (90%) + Co (10%), and the molding face is mirror finished to 0.01 μm or less in terms of Rmax. The surface of the substrate 1 comprising Si fitted to the mold is polished similarly to $\text{Rmax} < 0.01 \mu\text{m}$. Next, said substrate 1 is placed in a solution of diamond abrasive particles with an average particle size of 10 to 15 μm dispersed in ethyl alcohol, and damaging treatment is applied on its</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>surface by sonication vibration for 1.5 hours. The surface roughness of this substrate is measured to be $R_{max}=0.10\text{ }\mu\text{m}$. Next, by means of the microwave plasma CVD device shown in FIG. 6, first evacuation is effected to 1×10^{-7} Torr by the evacuation system 2, and then the gasses are delivered through the gas feeding system 3 into the reaction chamber at $\text{CH}_4=0.8\text{ SCCM}$ and $\text{H}_2=99.2\text{ SCCM}$ to make the pressure in the reaction chamber 40 Torr. Next, by use of the microwave 4 of 2.45 GHz with the power of microwave being made 450 W, a diamond polycrystalline film with a thickness of about $10\text{ }\mu\text{m}$ is formed on the Si substrate. At this time, the substrate temperature is made 850°C. The surface roughness of the diamond thin film obtained is measured by a contact needle type surface roughness meter to be $0.6\text{ }\mu\text{m}$ of R_{max}. Here, with the diamond thin film of $1\text{ }\mu\text{m}$ thickness formed under the same conditions, it is a polycrystalline film with an average particle size of $0.3\text{ }\mu\text{m}$ to $0.4\text{ }\mu\text{m}$ and a nucleation density of 6 to $9\text{ }\mu\text{m}^{-2}$. Next, after Ti is formed to about $3\text{ }\mu\text{m}$ by sputtering on the diamond thin film, Ag is formed to about $3\text{ }\mu\text{m}$ according to vacuum vapor deposition. Similarly, after Ni is formed to about $3\text{ }\mu\text{m}$ on the mold surface by ion plating, Ag is formed to about $3\text{ }\mu\text{m}$ by vacuum vapor deposition. After the substrate and the mold matrix are fitted together, heating is effected in vacuum at 850°C. to bond the substrate and the mold matrix. Here, bonding between the substrate and the mold matrix is effected by fixing under a uniform force of about 0.15 kg/mm^2 for about 3 hours.</p> <p>('349 patent at 18:27-65).</p>
<u>Claim 26</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from $50\text{ }\text{\AA}$ to $8000\text{ }\text{\AA}$.</p>	<p>The bonding agent in this case is formed by vacuum vapor deposition, sputtering, ion plating or plating. The film thickness of the bonding agent may be such that the unevenness of the surface of the diamond mm can be flattened on the diamond mm side, and adhesion is not lowered through internal stress of the film, namely generally within the range of $1\text{ }\mu\text{m}$ to $10\text{ }\mu\text{m}$, preferably $2\text{ }\mu\text{m}$ to $4\text{ }\mu\text{m}$.</p> <p>('349 patent at 7:13-20).</p> <p>Next, by use of the microwave 203 of 2.45 GHz, a diamond polycrystalline film with a thickness of $5\text{ }\mu\text{m}$ is formed on the mold matrix with the power of the microwave being 400 W.</p> <p>('349 patent at 14:21-25).</p> <p>By use of the mold matrix as described above, by means of the microwave plasma CVD device shown in FIG. 6, evacuation is effected similarly, and then through the gas feeding system 202, CH_4</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	is flowed at 0.5 SCCM and H ₂ at 99.5 SCCM, to make the pressure in the reaction chamber 35 Torr, and a diamond thin film a thickness of about 5 μm is formed on the mold matrix by microwave discharging under the same conditions. ('349 patent at 14:46-54).
<u>Claim 27</u>	
The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.	<p>The bonding agent in this case is formed by vacuum vapor deposition, sputtering, ion plating or plating. The film thickness of the bonding agent may be such that the unevenness of the surface of the diamond mm can be flattened on the diamond mm side, and adhesion is not lowered through internal stress of the film, namely generally within the range of 1 to 10 μm, preferably 2 to 4 μm. ('349 patent at 7:13-20).</p> <p>Next, by use of the microwave 203 of 2.45 GHz, a diamond polycrystalline film with a thickness of 5 μm is formed on the mold matrix with the power of the microwave being 400 W. ('349 patent at 14:21-25).</p> <p>By use of the mold matrix as described above, by means of the microwave plasma CVD device shown in FIG. 6, evacuation is effected similarly, and then through the gas feeding system 202, CH₄ is flowed at 0.5 SCCM and H₂ at 99.5 SCCM, to make the pressure in the reaction chamber 35 Torr, and a diamond thin film a thickness of about 5 μm is formed on the mold matrix by microwave discharging under the same conditions. ('349 patent at 14:46-54).</p>
<u>Claim 28</u>	
The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.	<p>First, the substrate surface is mirror polished to a surface roughness, which is preferably 0.05 μm or less in terms of Rmax, more preferably 0.01 μm or less. Next, diamond abrasive particles with an average particle size of 10 to 20 μm are dispersed in an alcohol, the above substrate is placed in this solution and then the solution is subjected to sonication vibration, thereby effecting fine damaging treatment on the substrate surface.</p> <p>During this operation, it is preferable to optimize the conditions for damaging treatment so that the surface roughness of the substrate surface may not exceed 0.05 82 m in terms of Rmax. Thereafter, a diamond thin film is formed to several μm to some 100 μm by the microwave plasma CVD method, the hot filament CVD method, the plasma jet method, the ECR plasma CVD method, etc. The gases employed at this time may be carbon containing gases, including hydrocarbons such as methane, ethane, propane, ethylene, benzene, acetylene, etc.; halogenated carbons such as methylene chloride,</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>carbon tetrachloride, chloroform, trichloroethane, etc.; alcohols such as methyl alcohol, ethyl alcohol, etc.; ketones such as (CH₃)₂, (C₆H₅)CO, etc.; gases such as CO, CO₂, etc. and mixtures of these gases with gases such as N₂, H₂, O₂, H₂O, Ar, etc. ('349 patent at 6:22-46).</p> <p>Next, the surface of the diamond film formed bonded onto the mold surface of a material which can easily be precisely worked as the matrix of mold for press molding and has heat resistance and hot impact resistance, such as tungsten carbide, thermet, zirconia, etc. The bonding agent in this case may be preferably one which is good in wettability with diamond and can assure sufficient mechanical strength and geometrical dimensional precision under the conditions (heating temperature, pressing pressure, etc.) of optical element molding. As such material, there may be included elements such as Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, AU, Si, Ge, Sn, Pb, etc., or compounds, mixtures of one kind or two or more kinds of these, or alloys such as Ag-Cu, Ag-Sn, Ti-Ag, Ti-Cu, Ti-Co, Ti-Ni, Au-Nb, Au-Ta, etc. ('349 patent at 6:47-64).</p> <p>Also, on the mold matrix to be bonded, a bonding agent layer for solid phase bonding is formed. The bonding agent may be preferably one which has good adhesion to the mold matrix and sufficient strength by bonding, and at the same time sufficient bonding strength under the conditions (heating temperature, pressing pressure, etc.) of optical element molding.</p> <p>Particularly, it is critical that it should have a thermal expansion coefficient approximate to the both. For example, when the mold matrix is made of tungsten carbide, Ti, Ta, Ni, etc. are suitable. In carrying out bonding, it is preferable to use the same kind of material for the film on the diamond film and the mm on the mold matrix and bond the diamond film onto the mold matrix by solid phase mutually bonding between the same kind of materials.</p> <p>The bonding agent in this case is formed by vacuum vapor deposition, sputtering, ion plating or plating. The film thickness of the bonding agent may be such that the unevenness of the surface of the diamond mm can be flattened on the diamond mm side, and adhesion is not lowered through internal stress of the film, namely generally within the range of 1 to 10 μm, preferably 2 to 4 μm. Also, the film thickness of the film on the mold matrix and the layer participating in solid phase bonding, namely the solid phase bonding layer may be equal to this. Next, for effecting solid phase bonding, pressing may be carried out in vacuum higher than 1 X 10⁻⁴ Torr, at a</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>bonding temperature of 700° to 900° C. and pressure of 0.1 to 10 kg/cm². The press time in this case, which may differ on the plane precision of the bonding face, etc., may be about 30 minutes to 3 hours. The solid phase bonding is not necessarily effected mutually between the same kind of materials but different kinds of materials may be employed. However, in the latter case, the film thickness range from 100 μm to 1 mm, and the bonding temperature, the pressig pressure, the pressing time, etc. are higher or longer than the case of the same kind of materials. ('349 patent at 6:65-7:36).</p> <p>After the diamond film is bonded onto the mold matrix the substrate used for formation of the diamond film is removed by polishing or etching. As a result, the diamond film can be formed as reversed on the mold matrix. Since the surface of the diamond film has the shape of the substrate surface transferred thereon, it is very smooth as different from the surface inherent in the diamond film, and its surface roughness can be made 0.05 μm or less in terms of Rmax. However, when the mold shape is slipped from the desired shape by bonding or when the surface roughness exceeds 0.05 μm in terms of Rmax, the shape and the surface roughness can be modified to desired ones by use of the polishing method of diamond single crystal generally known in the art. ('349 patent at 7:37-50).</p> <p>By means of the microwave plasma CVD device shown in FIG. 6, a diamond thin film is precipitated to 5 μm on a mold matrix comp;rising WC-10% Co. At this time, the surface of the mold matrix is subjected to the damaging treatment after the mirror surface working of the molding face shape in a sonication washer in a solution of diamond abrasive particles with a particle size of 15 μm dispersed in ethyl alcohol for one hour in order to enhance diamond nucleation density. Depending on the extent of mirror surface working, no damaging treatment as mentioned above may be performed. Formation of the diamond thin film is performed by means of the microwave plasma CVD device shown in FIG. 6 by first evacuating to 1 X 10⁻⁷ Torr by the evacuation system 201, and then delivering the gases from the gas feeding system 202 at the flow rates of CH₄=2 SCCM, H₂=98 SCCM to the reaction chamber to make the pressure in the reaction chamber 35 Torr. Next, by use of the microwave 203 of 2.45 GHz, a diamond polycrystalline film with a thickness of 5 μm is formed on the mold matrix with the power of the microwave being 400 W. At this time, the temperature of the mold matrix is made 850° C. The surface roughness of the diamond thin</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>film obtained is measured by a contact needle type surface roughness meter to be 0.3 μm of R_{max}. It is also conformed by X-ray diffraction that the (100) face is oriented substantially in parallel to the substrate surface. ('349 patent at 14:3-30).</p> <p>By use of the mold matrix as described above, by means of the microwave plasma CVD device shown in FIG. 6, evacuation is effected similarly, and then through the gas feeding system 202, CH_4 is flowed at 0.5 SCCM and H_2 at 99.5 SCCM, to make the pressure in the reaction chamber 35 Torr, and a diamond thin film a thickness of about 5 μm is formed on the mold matrix by microwave discharging under the same conditions. At this time, the temperature of the mold matrix is 850°C. The surface roughness of the film obtained is 1 μm in terms of R_{max}. By X-ray diffraction, (111), (110) peaks are obtained, and particularly it is found to be a film composed mainly of the (111) face. Next, when the film surface is polished similarly as described above, the surface roughness of the film surface after polishing is 0.05 μm in terms of R_{max} and the film thickness 3 μm. The polishing speed at this time is 0.4 $\mu\text{m}/\text{h}$. ('349 patent at 14:47-63).</p> <p>The mold for optical element molding shown in FIG. 9 comprises WC (90%) + Co (10%), and the molding face is mirror finished to 0.01 μm or less in terms of R_{max}. The surface of the substrate 1 comprising Si fitted to the mold is polished similarly to $R_{\text{max}} < 0.01 \mu\text{m}$. Next, said substrate 1 is placed in a solution of diamond abrasive particles with an average particle size of 10 to 15 μm dispersed in ethyl alcohol, and damaging treatment is applied on its surface by sonication vibration for 1.5 hours. The surface roughness of this substrate is measured to be $R_{\text{max}} = 0.10 \mu\text{m}$. Next, by means of the microwave plasma CVD device shown in FIG. 6, first evacuation is effected to 1×10^{-7} Torr by the evacuation system 2, and then the gasses are delivered through the gas feeding system 3 into the reaction chamber at $\text{CH}_4 = 0.8$ SCCM and $\text{H}_2 = 99.2$ SCCM to make the pressure in the reaction chamber 40 Torr. Next, by use of the microwave 4 of 2.45 GHz with the power of microwave being made 450 W, a diamond polycrystalline film with a thickness of about 10 μm is formed on the Si substrate. At this time, the substrate temperature is made 850° C. The surface roughness of the diamond thin film obtained is measured by a contact needle type surface roughness meter to be 0.6 μm of R_{max}. Here, with the diamond thin film of 1 μm thickness formed under the same conditions, it is a polycrystalline film with an average particle size of</p>

'086 Patent	U.S. Patent No. 5,380,349 ("349 Patent")
	<p>0.3 μm to 0.4 μm and a nucleation density of 6 to 9 μm^{-2}. Next, after Ti is formed to about 3 μm by sputtering on the diamond thin film, Ag is formed to about 3 μm according to vacuum vapor deposition. Similarly, after Ni is formed to about 3 μm on the mold surface by ion plating, Ag is formed to about 3μm by vacuum vapor deposition. After the substrate and the mold matrix are fitted together, heating is effected in vacuum at 850$^{\circ}$C. to bond the substrate and the mold matrix. Here, bonding between the substrate and the mold matrix is effected by fixing under a uniform force of about 0.15 kg/mm2 for about 3 hours.</p> <p>('349 patent at 18:27-65).</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>U.S. Patent No. 5,707,717 was filed on March 10, 1994, and is continuation-in-part of an application published October 15, 1992, U.S. App. Ser. No. 07/961,222. Moreover, its two Japanese priority applications published as Japanese Kokai Publication Nos. 05-117087 and 05-117856, respectively, on May 14, 1993, more than a year before the U.S. filing date of the '086 patent.</p> <p>Elements below show hard carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>This invention relates to a technique of improving the adhesion or binding properties of a diamond-like thin film with respect to slightly adhesive substrates of articles, such as metallic mold substrates of hardened steel. ('717 Patent at 1:9-12).</p> <p>A protectively coated article comprises a substrate of a material selected from the group consisting of alloys containing at least Co, Ni, or Fe, ceramics, and glass and which has only a slight affinity for a diamond-like thin film, an intermediate carbon layer formed on the substrate, the intermediate layer having a hardness Hv in the range from 1000 to 5000 kg/mm², or harder than the substrate but less hard than a diamond-like thin film to be formed thereon, and a diamond-like thin film formed further thereon. The interposition of the intermediate layer permits the diamond-like thin film to be bound securely to a substrate surface which has a slight affinity for the film. ('717 Patent, Abstract).</p> <p>The diamond-like thin films are capable of being bound solidly to substrates of silicon or the like. However, they are not as adhesive to certain types of article substrates and have a common problem of easily coming off from those substrate surfaces upon subjection to external forces. The shortcoming makes the films unable to be fully effective as protective coatings for applications where corrosion resistance or wear resistance is of essential importance. In particular, Fe metals and alloys (e.g., soft steel "STC", stainless steel, and hardened steels "SKD", "SKS"), alloys of other metals such as Co and Ni, glass, and ceramics are known to produce weak bonds between themselves and diamond-like thin</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
	<p>films. (‘717 Patent at 1:38-49).</p> <p>None of these printed publications of the prior art suggest that the use of a low-hardness carbonaceous film as an intermediate layer makes it possible to form an excellently adherent and hard diamond-like film on a bulk metal such as stainless steel or steel containing Fe, Co, etc. (‘717 Patent at 3:17-20).</p> <p>The invention provides protectively coated articles comprising a substrate of ordinary character, of course, or a substrate, such as of a metallic mold, selected from the group consisting of alloys, e.g., a hardened steel, which contain at least Co, Ni, or Fe, ceramics, and glass, the substrate having a slight affinity for a diamond-like thin film, an intermediate carbon layer formed on the substrate surface, the intermediate layer having a hardness Hv in the range from 1000 to 5000 kg/mm², or harder than the substrate but less hard than a diamond-like thin film to be formed thereon, and a diamond-like thin film formed as the outer layer. (‘717 Patent at 3:50-60).</p> <p>By ionization evaporation were formed intermediate layers on substrates of articles made of SKD11 (hardened steel), SKS2 (hardened steel), and quartz glass ("SUPRASL", the trade designation of a Shin-Etsu Quartz product) under the conditions given in Table 1 and then formed thereon diamond-like thin films again under the conditions given in Table 1. (‘717 Patent at 6:26-31).</p> <p>The intermediate layer according to the invention makes it possible to apply a diamond-like thin film to the substrates of molds and other articles normally difficult to bind with it and thereby substantially improve the durability of the articles. (‘717 Patent at 7:40-44).</p> <p>A protectively coated article which comprises a substrate of a material selected from the group consisting of alloys containing at least Co, Ni, or Fe, ceramics, and glass and which has only a slight affinity for a diamond-like thin film...</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
	<p>(‘717 Patent at 7:46-48; 8:19-20).</p> <p>See U.S. App. Ser. No. 07/961,222 at pages 1, 2, 6 7, 8, 14, 18, and 19 (containing analogous disclosures).</p> <p>JP ‘087 at [0001], [0003], [0007], [0015], [0019], claim 2, and Abstract (containing analogous disclosures).</p>
<p>an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and</p>	<p>A protectively coated article comprises a substrate of a material selected from the group consisting of alloys containing at least Co, Ni, or Fe, ceramics, and glass and which has only a slight affinity for a diamond-like thin film, an intermediate carbon layer formed on the substrate, the intermediate layer having a hardness Hv in the range from 1000 to 5000 kg/mm², or harder than the substrate but less hard than a diamond-like thin film to be formed thereon, and a diamond-like thin film formed further thereon. The interposition of the intermediate layer permits the diamond-like thin film to be bound securely to a substrate surface which has a slight affinity for the film. (‘717 Patent, Abstract).</p> <p>None of these printed publications of the prior art suggest that the use of a low-hardness carbonaceous film as an intermediate layer makes it possible to form an excellently adherent and hard diamond-like film on a bulk metal such as stainless steel or steel containing Fe, Co, etc. (‘717 Patent at 3:17-20).</p> <p>The invention provides protectively coated articles comprising a substrate of ordinary character, of course, or a substrate, such as of a metallic mold, selected from the group consisting of alloys, e.g., a hardened steel, which contain at least Co, Ni, or Fe, ceramics, and glass, the substrate having a slight affinity for a diamond-like thin film, an intermediate carbon layer formed on the substrate surface, the intermediate layer having a hardness Hv in the range from 1000 to 5000 kg/mm², or harder than the substrate but less hard than a diamond-like thin film to be formed thereon, and a diamond-like thin film formed as the outer layer. (‘717 Patent at 3:50-60).</p> <p>According to this invention, a substrate is coated with an</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
	<p>intermediate carbon layer having a greater hardness than the substrate but less than that of the diamond-like thin film to be formed thereon, through control of the deposition conditions of ionization evaporation, and then the diamond-like thin film is formed without changing the material hydrocarbon and using the same ionization evaporation technique excepting changes in the film-forming conditions. ('717 Patent at 4:3-10).</p> <p>According to the method, the formation of the intermediate layer is immediately followed by that of a diamond-like thin film without exposing the intermediate layer or interrupting the operation but by simply altering the film-forming conditions for the fabrication of the diamond-like film. ('717 Patent at 4:19-23).</p> <p>Both the intermediate layer and the diamond-like thin film can be formed using the same ionization evaporation apparatus and from the same material, with the only exception that the evaporation conditions are changed continuously or stepwise. ('717 Patent at 4:38-43).</p> <p>The intermediate layer can be formed by the film-forming procedure for the diamond-like thin film with the exception that film-forming energy level is lowered. ('717 Patent at 5:19-22).</p> <p>By ionization evaporation were formed intermediate layers on substrates of articles made of SKD11 (hardened steel), SKS2 (hardened steel), and quartz glass ("SUPRASL", the trade designation of a Shin-Etsu Quartz product) under the conditions given in Table 1 and then formed thereon diamond-like thin films again under the conditions given in Table 1. ('717 Patent at 6:26-31).</p> <p>The intermediate layer according to the invention makes it possible to apply a diamond-like thin film to the substrates of molds and other articles normally difficult to bind with it and thereby substantially improve the durability of the articles. ('717 Patent at 7:40-44).</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
	<p>A protectively coated article which comprises a substrate of a material selected from the group consisting of alloys containing at least Co, Ni, or Fe, ceramics, and glass and which has only a slight affinity for a diamond-like thin film, an intermediate layer formed on the substrate consisting essentially of carbon,... (‘717 Patent at 7:46-48; 8:19-21).</p> <p>See U.S. App. Ser. No. 07/961,222 at pages 6, 7, 8, 9, 10, 11, 14, 18, and 19 (containing analogous disclosures).</p> <p>JP ‘087 at [0007], [0008], [0010], [0015], [0019], claims 1-2, and Abstract (containing analogous disclosures).</p>
a hard carbon film arranged on said intermediate layer.	<p>The diamond-like thin films are capable of being bound solidly to substrates of silicon or the like. However, they are not as adhesive to certain types of article substrates and have a common problem of easily coming off from those substrate surfaces upon subjection to external forces. The shortcoming makes the films unable to be fully effective as protective coatings for applications where corrosion resistance or wear resistance is of essential importance. In particular, Fe metals and alloys (e.g., soft steel "STC", stainless steel, and hardened steels "SKD", "SKS"), alloys of other metals such as Co and Ni, glass, and ceramics are known to produce weak bonds between themselves and diamond-like thin films. Iron-based substrates, such as structural and sliding parts, are of the highest industrial utility. Glass and ceramics too have a broad range of applications including sliding members of thermal heads. It is therefore important to improve the adhesiveness of diamond-like thin films to these substrate surfaces on which they are to be formed. (‘717 Patent at 1:38-49).</p> <p>It is therefore an object of the present invention to provide in a relatively simple way articles protected with a diamond-like thin film which is strongly bound to and highly adhesive to the substrate and exhibits improved peeling resistance and durability. (‘717 Patent at 3:33-37).</p> <p>A protectively coated article comprises a substrate of a material selected from the group consisting of alloys containing at least Co, Ni, or Fe, ceramics, and glass and</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
	<p>which has only a slight affinity for a diamond-like thin film, an intermediate carbon layer formed on the substrate, the intermediate layer having a hardness Hv in the range from 1000 to 5000 kg/mm², or harder than the substrate but less hard than a diamond-like thin film to be formed thereon, and a diamond-like thin film formed further thereon. The interposition of the intermediate layer permits the diamond-like thin film to be bound securely to a substrate surface which has a slight affinity for the film. (717 Patent, Abstract).</p> <p>None of these printed publications of the prior art suggest that the use of a low-hardness carbonaceous film as an intermediate layer makes it possible to form an excellently adherent and hard diamond-like film on a bulk metal such as stainless steel or steel containing Fe, Co, etc. (717 Patent at 3:17-20).</p> <p>The invention provides protectively coated articles comprising a substrate of ordinary character, of course, or a substrate, such as of a metallic mold, selected from the group consisting of alloys, e.g., a hardened steel, which contain at least Co, Ni, or Fe, ceramics, and glass, the substrate having a slight affinity for a diamond-like thin film, an intermediate carbon layer formed on the substrate surface, the intermediate layer having a hardness Hv in the range from 1000 to 5000 kg/mm², or harder than the substrate but less hard than a diamond-like thin film to be formed thereon, and a diamond-like thin film formed as the outer layer. (717 Patent at 3:50-60).</p> <p>According to this invention, a substrate is coated with an intermediate carbon layer having a greater hardness than the substrate but less than that of the diamond-like thin film to be formed thereon, through control of the deposition conditions of ionization evaporation, and then the diamond-like thin film is formed without changing the material hydrocarbon and using the same ionization evaporation technique excepting changes in the film-forming conditions. (717 Patent at 4:3-10).</p> <p>Both the intermediate layer and the diamond-like thin film can be formed using the same ionization evaporation</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
	<p>apparatus and from the same material, with the only exception that the evaporation conditions are changed continuously or stepwise. (‘717 Patent at 4:38-43).</p> <p>The hardness of the diamond-like thin film formed by ionization evaporation is about 6000 kg/mm² or above. (‘717 Patent at 4:47-48).</p> <p>By ionization evaporation were formed intermediate layers on substrates of articles made of SKD11 (hardened steel), SKS2 (hardened steel), and quartz glass ("SUPRASL", the trade designation of a Shin-Etsu Quartz product) under the conditions given in Table 1 and then formed thereon diamond-like thin films again under the conditions given in Table 1. (‘717 Patent at 6:26-31).</p> <p>A protectively coated article which comprises...a diamond-like thin film consisting of amorphous carbon... (‘717 Patent at 7:46 and 8:25-26).</p> <p>See U.S. App. Ser. No. 07/961,222 at pages 1, 2, 6 7, 8, 10, 14, and 19 (containing analogous disclosures).</p> <p>JP ‘087 at [0003], [0007], [0008], [0010], [0015], and Abstract (containing analogous disclosures).</p>
<u>Claim 26</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p>The thickness of the intermediate layer is desirably between 0.02 to 3.0 μm, more desirably between 0.05 and 0.5 μm. (‘717 Patent at 4:43-45).</p> <p>said intermediate layer having a thickness of 0.02 to 3.0 μm. (‘717 Patent at 8:25-26).</p> <p>the intermediate layer has a thickness of 0.05 to 0.5 μm. (‘717 Patent at 8:42-43).</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ('717 Patent')																																																																																																												
	<div>78</div> <table><tr><th colspan="4">Intermediate layer</th><th colspan="2">Diamond-like</th><th colspan="6">Substrate</th></tr><tr><th colspan="2">Substrate</th><th colspan="2">Diamond</th><th colspan="2">like</th><th colspan="6"></th></tr><tr><th colspan="2">side</th><th colspan="2">film side</th><th colspan="2">thin film</th><th colspan="2">SKD11</th><th colspan="2">Quartz glass</th><th colspan="2">SKS2</th></tr><tr><th>Thick-ness μm</th><th>Hard-ness Hv</th><th>Thick-ness μm</th><th>Hard-ness Hv</th><th>Thick-ness μm</th><th>Hard-ness Hv</th><th>Adhesion strength</th><th>Scratch hard-ness</th><th>Adhesion strength</th><th>Scratch hard-ness</th><th>Adhesion strength</th><th>Scratch hard-ness</th></tr><tr><td>Ex. 1</td><td>0.1</td><td>2500</td><td>—</td><td>—</td><td>3.0</td><td>6000</td><td>1.0</td><td>1.0</td><td>1.0</td><td>1.0</td><td>1.0</td></tr><tr><td>Ex. 2</td><td>0.1</td><td>2500</td><td>0.1</td><td>4000</td><td>3.0</td><td>6000</td><td>1.3</td><td>1.2</td><td>1.4</td><td>1.2</td><td>1.4</td></tr><tr><td>Ex. 3</td><td>0.03</td><td>3000</td><td>0.03</td><td>5000</td><td>3.0</td><td>5800</td><td>0.8</td><td>0.7</td><td>0.9</td><td>0.8</td><td>0.9</td></tr><tr><td>Ex. 4</td><td>0.01</td><td>2000</td><td>0.01</td><td>4000</td><td>3.0</td><td>5500</td><td>0.6</td><td>0.5</td><td>0.6</td><td>0.6</td><td>0.6</td></tr><tr><td>Comp. Ex.</td><td colspan="4">No intermediate layer</td><td>3.0</td><td>5400</td><td>0.1</td><td>0.2</td><td>0.09</td><td>0.08</td><td>0.1</td></tr></table>	Intermediate layer				Diamond-like		Substrate						Substrate		Diamond		like								side		film side		thin film		SKD11		Quartz glass		SKS2		Thick-ness μm	Hard-ness Hv	Thick-ness μm	Hard-ness Hv	Thick-ness μm	Hard-ness Hv	Adhesion strength	Scratch hard-ness	Adhesion strength	Scratch hard-ness	Adhesion strength	Scratch hard-ness	Ex. 1	0.1	2500	—	—	3.0	6000	1.0	1.0	1.0	1.0	1.0	Ex. 2	0.1	2500	0.1	4000	3.0	6000	1.3	1.2	1.4	1.2	1.4	Ex. 3	0.03	3000	0.03	5000	3.0	5800	0.8	0.7	0.9	0.8	0.9	Ex. 4	0.01	2000	0.01	4000	3.0	5500	0.6	0.5	0.6	0.6	0.6	Comp. Ex.	No intermediate layer				3.0	5400	0.1	0.2	0.09	0.08	0.1
Intermediate layer				Diamond-like		Substrate																																																																																																							
Substrate		Diamond		like																																																																																																									
side		film side		thin film		SKD11		Quartz glass		SKS2																																																																																																			
Thick-ness μm	Hard-ness Hv	Thick-ness μm	Hard-ness Hv	Thick-ness μm	Hard-ness Hv	Adhesion strength	Scratch hard-ness	Adhesion strength	Scratch hard-ness	Adhesion strength	Scratch hard-ness																																																																																																		
Ex. 1	0.1	2500	—	—	3.0	6000	1.0	1.0	1.0	1.0	1.0																																																																																																		
Ex. 2	0.1	2500	0.1	4000	3.0	6000	1.3	1.2	1.4	1.2	1.4																																																																																																		
Ex. 3	0.03	3000	0.03	5000	3.0	5800	0.8	0.7	0.9	0.8	0.9																																																																																																		
Ex. 4	0.01	2000	0.01	4000	3.0	5500	0.6	0.5	0.6	0.6	0.6																																																																																																		
Comp. Ex.	No intermediate layer				3.0	5400	0.1	0.2	0.09	0.08	0.1																																																																																																		
	<p>(‘717 Patent at Columns 7-8).</p> <p>See U.S. App. Ser. No. 07/961,222 at pages 10, 17, and 19 (containing analogous disclosures).</p> <p>JP ‘087 at [0010], [0018], and claim 5 (containing analogous disclosures).</p>																																																																																																												
Claim 27																																																																																																													
The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.	<p>The thickness of the intermediate layer is desirably between 0.02 to 3.0 μm, more desirably between 0.05 and 0.5 μm. (‘717 Patent at 4:43-45).</p> <p>said intermediate layer having a thickness of 0.02 to 3.0 μm. (‘717 Patent at 8:25-26).</p> <p>the intermediate layer has a thickness of 0.05 to 0.5 μm. (‘717 Patent at 8:42-43).</p> <div>78</div> <table><tr><th colspan="4">Intermediate layer</th><th colspan="2">Diamond-like</th><th colspan="6">Substrate</th></tr><tr><th colspan="2">Substrate</th><th colspan="2">Diamond</th><th colspan="2">like</th><th colspan="6"></th></tr><tr><th colspan="2">side</th><th colspan="2">film side</th><th colspan="2">thin film</th><th colspan="2">SKD11</th><th colspan="2">Quartz glass</th><th colspan="2">SKS2</th></tr><tr><th>Thick-ness μm</th><th>Hard-ness Hv</th><th>Thick-ness μm</th><th>Hard-ness Hv</th><th>Thick-ness μm</th><th>Hard-ness Hv</th><th>Adhesion strength</th><th>Scratch hard-ness</th><th>Adhesion strength</th><th>Scratch hard-ness</th><th>Adhesion strength</th><th>Scratch hard-ness</th></tr><tr><td>Ex. 1</td><td>0.1</td><td>2500</td><td>—</td><td>—</td><td>3.0</td><td>6000</td><td>1.0</td><td>1.0</td><td>1.0</td><td>1.0</td><td>1.0</td></tr><tr><td>Ex. 2</td><td>0.1</td><td>2500</td><td>0.1</td><td>4000</td><td>3.0</td><td>6000</td><td>1.3</td><td>1.2</td><td>1.4</td><td>1.2</td><td>1.4</td></tr><tr><td>Ex. 3</td><td>0.03</td><td>3000</td><td>0.03</td><td>5000</td><td>3.0</td><td>5800</td><td>0.8</td><td>0.7</td><td>0.9</td><td>0.8</td><td>0.9</td></tr><tr><td>Ex. 4</td><td>0.01</td><td>2000</td><td>0.01</td><td>4000</td><td>3.0</td><td>5500</td><td>0.6</td><td>0.5</td><td>0.6</td><td>0.6</td><td>0.6</td></tr><tr><td>Comp. Ex.</td><td colspan="4">No intermediate layer</td><td>3.0</td><td>5400</td><td>0.1</td><td>0.2</td><td>0.09</td><td>0.08</td><td>0.1</td></tr></table>	Intermediate layer				Diamond-like		Substrate						Substrate		Diamond		like								side		film side		thin film		SKD11		Quartz glass		SKS2		Thick-ness μm	Hard-ness Hv	Thick-ness μm	Hard-ness Hv	Thick-ness μm	Hard-ness Hv	Adhesion strength	Scratch hard-ness	Adhesion strength	Scratch hard-ness	Adhesion strength	Scratch hard-ness	Ex. 1	0.1	2500	—	—	3.0	6000	1.0	1.0	1.0	1.0	1.0	Ex. 2	0.1	2500	0.1	4000	3.0	6000	1.3	1.2	1.4	1.2	1.4	Ex. 3	0.03	3000	0.03	5000	3.0	5800	0.8	0.7	0.9	0.8	0.9	Ex. 4	0.01	2000	0.01	4000	3.0	5500	0.6	0.5	0.6	0.6	0.6	Comp. Ex.	No intermediate layer				3.0	5400	0.1	0.2	0.09	0.08	0.1
Intermediate layer				Diamond-like		Substrate																																																																																																							
Substrate		Diamond		like																																																																																																									
side		film side		thin film		SKD11		Quartz glass		SKS2																																																																																																			
Thick-ness μm	Hard-ness Hv	Thick-ness μm	Hard-ness Hv	Thick-ness μm	Hard-ness Hv	Adhesion strength	Scratch hard-ness	Adhesion strength	Scratch hard-ness	Adhesion strength	Scratch hard-ness																																																																																																		
Ex. 1	0.1	2500	—	—	3.0	6000	1.0	1.0	1.0	1.0	1.0																																																																																																		
Ex. 2	0.1	2500	0.1	4000	3.0	6000	1.3	1.2	1.4	1.2	1.4																																																																																																		
Ex. 3	0.03	3000	0.03	5000	3.0	5800	0.8	0.7	0.9	0.8	0.9																																																																																																		
Ex. 4	0.01	2000	0.01	4000	3.0	5500	0.6	0.5	0.6	0.6	0.6																																																																																																		
Comp. Ex.	No intermediate layer				3.0	5400	0.1	0.2	0.09	0.08	0.1																																																																																																		
	<p>(‘717 Patent at Columns 7-8).</p> <p>See U.S. App. Ser. No. 07/961,222 at pages 10, 17, and 19</p>																																																																																																												

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
	(containing analogous disclosures). JP '087 at [0010], [0018], and claim 5 (containing analogous disclosures).
<u>Claim 28</u>	
The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.	<p>The diamond-like thin films are capable of being bound solidly to substrates of silicon or the like. However, they are not as adhesive to certain types of article substrates and have a common problem of easily coming off from those substrate surfaces upon subjection to external forces. The shortcoming makes the films unable to be fully effective as protective coatings for applications where corrosion resistance or wear resistance is of essential importance. In particular, Fe metals and alloys (e.g., soft steel "STC", stainless steel, and hardened steels "SKD", "SKS"), alloys of other metals such as Co and Ni, glass, and ceramics are known to produce weak bonds between themselves and diamond-like thin films. Iron-based substrates, such as structural and sliding parts, are of the highest industrial utility. Glass and ceramics too have a broad range of applications including sliding members of thermal heads. It is therefore important to improve the adhesiveness of diamond-like thin films to these substrate surfaces on which they are to be formed. ('717 Patent at 1:38-49).</p> <p>It is therefore an object of the present invention to provide in a relatively simple way articles protected with a diamond-like thin film which is strongly bound to and highly adhesive to the substrate and exhibits improved peeling resistance and durability. ('717 Patent at 3:33-37).</p> <p>A protectively coated article comprises a substrate of a material selected from the group consisting of alloys containing at least Co, Ni, or Fe, ceramics, and glass and which has only a slight affinity for a diamond-like thin film, an intermediate carbon layer formed on the substrate, the intermediate layer having a hardness Hv in the range from 1000 to 5000 kg/mm², or harder than the substrate but less hard than a diamond-like thin film to be formed thereon, and a diamond-like thin film formed further thereon. The interposition of the intermediate layer permits the diamond-like thin film to be bound securely to a substrate surface</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
	<p>which has a slight affinity for the film. (‘717 Patent, Abstract).</p> <p>None of these printed publications of the prior art suggest that the use of a low-hardness carbonaceous film as an intermediate layer makes it possible to form an excellently adherent and hard diamond-like film on a bulk metal such as stainless steel or steel containing Fe, Co, etc. (‘717 Patent at 3:17-20).</p> <p>The invention provides protectively coated articles comprising a substrate of ordinary character, of course, or a substrate, such as of a metallic mold, selected from the group consisting of alloys, e.g., a hardened steel, which contain at least Co, Ni, or Fe, ceramics, and glass, the substrate having a slight affinity for a diamond-like thin film, an intermediate carbon layer formed on the substrate surface, the intermediate layer having a hardness Hv in the range from 1000 to 5000 kg/mm², or harder than the substrate but less hard than a diamond-like thin film to be formed thereon, and a diamond-like thin film formed as the outer layer. (‘717 Patent at 3:50-60).</p> <p>According to this invention, a substrate is coated with an intermediate carbon layer having a greater hardness than the substrate but less than that of the diamond-like thin film to be formed thereon, through control of the deposition conditions of ionization evaporation, and then the diamond-like thin film is formed without changing the material hydrocarbon and using the same ionization evaporation technique excepting changes in the film-forming conditions. (‘717 Patent at 4:3-10).</p> <p>Both the intermediate layer and the diamond-like thin film can be formed using the same ionization evaporation apparatus and from the same material, with the only exception that the evaporation conditions are changed continuously or stepwise. (‘717 Patent at 4:38-43).</p> <p>The hardness of the diamond-like thin film formed by ionization evaporation is about 6000 kg/mm² or above. (‘717 Patent at 4:47-48).</p>

'086 Patent	U.S. Patent No. 5,707,717; Japanese Patent Application Publication No. 05-117087 ("717 Patent")
	<p>By ionization evaporation were formed intermediate layers on substrates of articles made of SKD11 (hardened steel), SKS2 (hardened steel), and quartz glass ("SUPRASL", the trade designation of a Shin-Etsu Quartz product) under the conditions given in Table 1 and then formed thereon diamond-like thin films again under the conditions given in Table 1. (717 Patent at 6:26-31).</p> <p>A protectively coated article which comprises...a diamond-like thin film consisting of amorphous carbon... (717 Patent at 7:46 and 8:25-26).</p> <p>See U.S. App. Ser. No. 07/961,222 at pages 1, 2, 6, 7, 8, 10, 14, and 19 (containing analogous disclosures).</p> <p>JP '087 at [0003], [0007], [0008], [0010], [0011], [0015], claim 1, and Abstract (containing analogous disclosures).</p>

'086 Patent	U.S. Patent No. 5,799,549 ("549 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The original parent application that eventually led to U.S. Patent No. 5,799,549 was filed on April 25, 1994, before the U.S. filing date of the '086 patent.</p> <p>Elements below show hard carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>A razor blade typically is formed of suitable substrate material such as metal or ceramic, and an edge is formed with wedge-shape configuration with an ultimate edge or tip that has a radius of less than about 1,000 angstroms, the wedge shaped surfaces having an included angle of less than 30°. ('549 Patent at 1:18-23).</p> <p>A diagrammatic view of the edge region of the blades 16, 20 and 44 is shown in FIG. 3, from which the aspect ratio may be better understood. The blade includes stainless steel body portion 50 with a wedge-shaped sharpened edge formed in a sequence of edge forming honing operations that forms a tip portion 52 that has a radius typically less than 500 angstroms with facets 54 and 56 that diverge at an angle of about 13°. ('549 Patent at 4:33-40).</p> <p>In one example of a particular processing sequence, a stack of blades 88 (2.5 centimeters long) is secured on the rotatable mount 86, the support cooling water is turned on, and the chamber 80 is evacuated. ('549 Patent at 5:39-42)</p>
an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and	<p>After the cleaning step, (i) the pressure in the chamber is adjusted to 0.1 millitorr of argon, (ii) the field coils 102 to a single duct 92 are energized, (iii) switch 120 to graphite target 96 is closed, (iv) the power supply 124 to the blades is adjusted to -1000 volts DC, and (v) an arc is struck/initiated on graphite target 96 with mechanical striker 98. The arc current is set to 100 A. An intense plasma of carbon ions is emitted from duct 92 and is deposited on the blades 88, which rotate 180 degrees every 10 seconds.</p> <p>After the arc has run for 2 minutes, the bias supply 124 is set to -50 volts and deposition continues for a total time of 16 minutes. ('549 Patent at 5:45-57).</p>

'086 Patent	U.S. Patent No. 5,799,549 ("549 Patent")
	<p>Process conditions include a multi-step bias to the substrate; an equal average deposition on both sides of the blade; and attention to the angle of presentation.</p> <p>An initial high bias in the range of 200-2000 volts is applied to the substrate during deposition for up to two minutes to establish adhesion. A second stage lower bias in the range of 10-200 volts is then applied to optimize the structure of the amorphous diamond hard carbon coating and to establish the desired crystal structure. Although at least the foregoing two stages are desirable according to this invention, it may also be desirable to provide a further "step down" incremental bias voltage reduction as, for example by adding an intermediate bias stage at 500 volts. (‘549 Patent at 6:42-55).</p>
a hard carbon film arranged on said intermediate layer.	<p>Improved razors and razor blades and processes for producing razor blades or similar cutting tools with sharp and durable cutting edges, by hard-carbon coating of blades with amorphous diamond, preferably using a filtered cathodic arc plasma source. (‘549 Patent at Abstract).</p> <p>According to this invention, the cutting edges of razor blades are provided with improved mechanical properties by applying to the sharpened edge of the substrate a coating of an amorphous diamond material. (‘549 Patent at 1:61-64).</p> <p>In accordance with another aspect of the invention, there is provided a process for forming a razor blade that includes the steps of providing a substrate; forming on an edge of the substrate a wedge-shaped sharpened edge that has an included angle of less than 30° and a tip radius (i.e. the estimated radius of the largest circle that may be positioned within the ultimate tip of the edge when such ultimate tip is viewed under a scanning electron microscope at magnifications of at least 25,000) preferably of less than 1,200 angstroms; and depositing, by filtered cathodic arc evaporation, a layer of amorphous diamond on the sharpened edge to provide a radius at the ultimate tip of the amorphous diamond layer of less than about 1000 angstroms. The amorphous diamond layer may be deposited by several</p>

'086 Patent	U.S. Patent No. 5,799,549 ("549 Patent")
	<p>techniques, all having in common the energetic deposition of carbon as a highly ionized species. (‘549 Patent at 2:59-3:7).</p> <p>Deposited on tip 52 and facets 54, 56 is amorphous diamond 60 that has a thickness of about 2,000 angstroms, with an aspect ratio (the ratio at distance (a) from amorphous diamond tip 70 to stainless steel tip 52, and the width (b) of the amorphous diamond coating 60 to tip 52) of about 3:1. (‘549 Patent at 4:40-45).</p> <p>Cathodic Arc Source. A deposition coating of amorphous diamond may be applied using conventional filtered cathodic arc plasma source material as described in U.S. Pat. No. 5,279,723 of Falabella et al. However, in a preferred embodiment, the deposition coating is applied according to the previously referenced co-pending application [USP 5480527] which is appended as Attachment A hereto. Although the rectangular source of Attachment A is particularly suited to the practice of this invention, the invention is not so limited. Likewise, an unfiltered or other conventional source may be used, and this invention should not be understood as being limited to filtered cathodic arc sources.</p> <p>Process Conditions and Adjustments. Process conditions include a multi-step bias to the substrate; an equal average deposition on both sides of the blade; and attention to the angle of presentation.</p> <p>An initial high bias in the range of 200-2000 volts is applied to the substrate during deposition for up to two minutes to establish adhesion. A second stage lower bias in the range of 10-200 volts is then applied to optimize the structure of the amorphous diamond hard carbon coating and to establish the desired crystal structure. (‘549 Patent at 6:22-51).</p> <p>It might be noted that the razor blades intended to be coated by this method are expected to be thinner than the usual razor blade, and sharper, and that the 2:1 and higher aspect ratios permitted by the process of this invention, coupled with the enormous strength of the amorphous diamond hard carbon coating, puts the blade in a class by itself.</p>

'086 Patent	U.S. Patent No. 5,799,549 ("549 Patent")
	('549 Patent at 7:51-57).
<u>Claim 26</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p>In a particular shaving unit, the razor blade structure includes two steel substrates, the wedge-shaped edges are disposed parallel to one another between the skin-engaging surfaces, the edge strengthening layer is of amorphous diamond with a thickness of about 1000 angstroms (typically a range of 400-2000 angstroms depending on substrate and processing parameters) and is characterized by at least 40 percent sp³ carbon bonding and a hardness of at least 45 gigapascals; and an adherent polymer coating is on each layer of amorphous diamond material. ('549 Patent at 3:38-47).</p> <p>Deposited on tip 52 and facets 54, 56 is amorphous diamond 60 that has a thickness of about 2,000 angstroms, with an aspect ratio (the ratio at distance (a) from amorphous diamond tip 70 to stainless steel tip 52, and the width (b) of the amorphous diamond coating 60 to tip 52) of about 3:1. ('549 Patent at 4:40-45).</p> <p>The resultant amorphous diamond blade coating is approximately 1000 angstroms in thickness on each facet. ('549 Patent at 5:58-61).</p>
<u>Claim 27</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.</p>	<p>In a particular shaving unit, the razor blade structure includes two steel substrates, the wedge-shaped edges are disposed parallel to one another between the skin-engaging surfaces, the edge strengthening layer is of amorphous diamond with a thickness of about 1000 angstroms (typically a range of 400-2000 angstroms depending on substrate and processing parameters) and is characterized by at least 40 percent sp³ carbon bonding and a hardness of at least 45 gigapascals; and an adherent polymer coating is on each layer of amorphous diamond material. ('549 Patent at 3:38-47).</p> <p>Deposited on tip 52 and facets 54, 56 is amorphous diamond 60 that has a thickness of about 2,000 angstroms, with an aspect ratio (the ratio at distance (a) from amorphous diamond tip 70 to stainless steel tip 52, and the width (b) of the amorphous diamond coating 60 to tip 52) of about 3:1.</p>

'086 Patent	U.S. Patent No. 5,799,549 ("549 Patent")
	<p>(‘549 Patent at 4:40-45).</p> <p>The resultant amorphous diamond blade coating is approximately 1000 angstroms in thickness on each facet. (‘549 Patent at 5:58-61).</p>
Claim 28	
<p>The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.</p>	<p>Improved razors and razor blades and processes for producing razor blades or similar cutting tools with sharp and durable cutting edges, by hard-carbon coating of blades with amorphous diamond, preferably using a filtered cathodic arc plasma source. (‘549 Patent at Abstract).</p> <p>According to this invention, the cutting edges of razor blades are provided with improved mechanical properties by applying to the sharpened edge of the substrate a coating of an amorphous diamond material. (‘549 Patent at 1:61-64).</p> <p>In accordance with another aspect of the invention, there is provided a process for forming a razor blade that includes the steps of providing a substrate; forming on an edge of the substrate a wedge-shaped sharpened edge that has an included angle of less than 30° and a tip radius (i.e. the estimated radius of the largest circle that may be positioned within the ultimate tip of the edge when such ultimate tip is viewed under a scanning electron microscope at magnifications of at least 25,000) preferably of less than 1,200 angstroms; and depositing, by filtered cathodic arc evaporation, a layer of amorphous diamond on the sharpened edge to provide a radius at the ultimate tip of the amorphous diamond layer of less than about 1000 angstroms. The amorphous diamond layer may be deposited by several techniques, all having in common the energetic deposition of carbon as a highly ionized species. (‘549 Patent at 2:59-3:7).</p> <p>Cathodic Arc Source. A deposition coating of amorphous diamond may be applied using conventional filtered cathodic arc plasma source material as described in U.S. Pat. No. 5,279,723 of Falabella et al. However, in a preferred embodiment, the deposition coating is applied according to the previously referenced co-pending application [USP</p>

'086 Patent	U.S. Patent No. 5,799,549 ("549 Patent")
	<p>5480527] which is appended as Attachment A hereto. Although the rectangular source of Attachment A is particularly suited to the practice of this invention, the invention is not so limited. Likewise, an unfiltered or other conventional source may be used, and this invention should not be understood as being limited to filtered cathodic arc sources.</p> <p>Process Conditions and Adjustments. Process conditions include a multi-step bias to the substrate; an equal average deposition on both sides of the blade; and attention to the angle of presentation.</p> <p>An initial high bias in the range of 200-2000 volts is applied to the substrate during deposition for up to two minutes to establish adhesion. A second stage lower bias in the range of 10-200 volts is then applied to optimize the structure of the amorphous diamond hard carbon coating and to establish the desired crystal structure. (‘549 Patent at 6:22-51).</p> <p>It might be noted that the razor blades intended to be coated by this method are expected to be thinner than the usual razor blade, and sharper, and that the 2:1 and higher aspect ratios permitted by the process of this invention, coupled with the enormous strength of the amorphous diamond hard carbon coating, puts the blade in a class by itself. (‘549 Patent at 7:51-57).</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The application that led to U.S. Patent No. 5,431,963 was filed on June 28, 1991, before the U.S. filing date of the '086 patent, or the filing dates of the Japanese applications to which the '086 patent claims priority.</p> <p>Elements below show a hard-carbon-film coated substrate.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>Magnetic tape cassettes, such as for audio and video tapes, are provided with guide pins and other guide members that come in sliding contact with the magnetic tapes to guide the running tape properly and ensure its stability during running. Those guides for video tape cassettes are made of stainless steel (of grade SUS 304 or the like), brass, or aluminum... ('543 Patent at 1:10-16.)</p> <p>For audio cassettes, guides of stainless steel or plastics such as polystyrene are used. ('543 Patent at 1:17-18.)</p> <p>The rotating hub 13 usually used is made of stainless steel (SUS 430) with or without plating (e.g., hard chromium plating). ('543 Patent at 1:59-61.)</p> <p>The concept of sliding members of the invention is applicable to magnetic tape guide members and contacting magnetic head surfaces of magnetic tape cassettes, disc-supporting rotating hubs of optical or magnetic disc devices and the like.</p> <p>With the structure described, the protective coating of sliding members used in recording-playback devices is solidly bound to the substrate with the aid of the anchor layer. Thus, the sliding members can be protectively coated with good productivity, attaining good resistance to friction and wear at low cost. ('543 Patent at 2:57-68.)</p> <p>A hub for a 3.5-in. disc shown in FIG. 1 was made. First, a blank hub of stainless steel was used (Comparative Example 1). ('543 Patent at 4:38-39.)</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
	<p>EXAMPLE 2 & COMPARATIVE EXAMPLE 3</p> <p>Using the hub of Comparative Example 1, the substrate was charged into the film-forming apparatus shown in FIG. 2. ('543 Patent at 7:10-13.)</p> <p>1. A sliding member provided with a protective film which comprises:</p> <p>a sliding member body made of a stainless steel; ('543 Patent, Claim 1)</p>
<p>an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and</p>	<p>A protectively coated sliding member comprises a sliding member body, an anchor layer formed thereon and which consists of (a) a hydrocarbon or hydrocarbon-based plasma polymer film, (b) a diamond-like film, or (c) an ion-plating film of a metal or metallic compound, and a protective coating formed on the anchor layer and which consists of a hydrocarbon or hydrocarbon-based plasma polymer film in case where the anchor layer consists of (a), a diamond or diamond-like film in case of (b), or an ion-plating film of a metallic compound in case of (c). The protective coating is of greater hardness than the anchor layer. ('543 Patent at Abstract.)</p> <p>The present invention is characterized in that an anchor layer consisting of a plasma polymer film of a hydrocarbon or hydrocarbon-based monomer, a diamond-like film, or anion plating film of a metal or metallic compound, and a protective coating consisting of a plasma polymer film of a hydrocarbon or hydrocarbon-based monomer of the same type as used in the anchor layer, a diamond or diamond-like film, or an ion plating film of a metallic compound, the protective coating being greater in hardness than the anchor layer, are provided on the surface of sliding members.</p> <p>When the protective coating consists of a plasma polymer film, the anchor layer is formed by plasma polymerization of a hydrocarbon or hydrocarbon-based monomer gas at a lower energy density than for the protective coating.</p> <p>When the protective coating is a diamond or diamond-like film, the anchor layer is formed under a set of conditions so chosen as to give a diamond-like film of lower density than</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
	<p>the protective coating. (‘543 Patent at 2:33-53.)</p> <p>An anchor layer is formed by varying the film-forming conditions, especially by decreasing the energy density. The resulting film has an H/C of from 1.5 to 2.0 and a low index of refraction. In this manner a soft anchor layer of low Vickers hardness is obtained. (‘543 Patent at 61-64.)</p> <p>The blank was placed in a plasma polymerizer, and a hydrocarbon polymer film was formed as an anchor layer on its surface at a pressure of 0.1 Torr, RF power of 350 W, and 20 SCCM CH₄. (‘543 Patent at 4:40-43.)</p> <p>An anchor layer is formed under mild conditions using a low energy, while a protective coating is produced with a high energy. The anchor layer film can be easily formed with lowered Va, Vd, and Vb. (‘543 Patent at 7:4-7.)</p> <p>Using the hub of Comparative Example 1, the substrate was charged into the film-forming apparatus shown in FIG. 2. The vacuum chamber 10 was evacuated to 10⁻⁶ Torr, and then methane gas was introduced. At a gas pressure of 10⁻¹ Torr, hot cathode filaments were allowed to cause an electric discharge. The magnetic flux density of the solenoid 39 was 400 gauss, the substrate voltage Va=200 V, Vd=30 V, and the substrate temperature 200° C. An alternating current If of 25 A was flown through the filaments 34.</p> <p>The filaments were in the form of coils 3 mm wide surrounded by an electrode with a spacing of 8 mm in between, and the feed rate was 40 mm/hr.</p> <p>Next, Va was changed to 450 V (the other conditions being left unchanged) and a diamond-like protective coating was made (Example 2). (‘543 Patent at 7:11-26.)</p> <p>[A]n anchor layer formed on the surface of the body, said anchor layer consisting of a film selected from the group of</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
	<p>(a) a hydrocarbon plasma polymer film consisting of carbon and hydrogen and having an H/C value of about 1.5 to about 2.0 and</p> <p>(b) a diamond film formed by ionization evaporation and having a vickers hardness of about 2,500 kg/mm²; and (543 Patent, Claim 1)</p>
a hard carbon film arranged on said intermediate layer.	<p>A protectively coated sliding member comprises a sliding member body, an anchor layer formed thereon and which consists of (a) a hydrocarbon or hydrocarbon-based plasma polymer film, (b) a diamond-like film, or (c) an ion-plating film of a metal or metallic compound, and a protective coating formed on the anchor layer and which consists of a hydrocarbon or hydrocarbon-based plasma polymer film in case where the anchor layer consists of (a), a diamond or diamond-like film in case of (b), or an ion-plating film of a metallic compound in case of (c). The protective coating is of greater hardness than the anchor layer. (543 Patent at Abstract.)</p> <p>The present invention is characterized in that an anchor layer consisting of a plasma polymer film of a hydrocarbon or hydrocarbon-based monomer, a diamond-like film, or an ion plating film of a metal or metallic compound, and a protective coating consisting of a plasma polymer film of a hydrocarbon or hydrocarbon-based monomer of the same type as used in the anchor layer, a diamond or diamond-like film, or an ion plating film of a metallic compound, the protective coating being greater in hardness than the anchor layer, are provided on the surface of sliding members.</p> <p>When the protective coating consists of a plasma polymer film, the anchor layer is formed by plasma polymerization of a hydrocarbon or hydrocarbon-based monomer gas at a lower energy density than for the protective coating.</p> <p>When the protective coating is a diamond or diamond-like film, the anchor layer is formed under a set of conditions so chosen as to give a diamond-like film of lower density than the protective coating. (543 Patent at 2:33-53.)</p> <p>To form a plasma polymer film on the surface of a sliding</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
	<p>member, any known monomer gas may be used as desired. Examples are hydrocarbon monomers, such as methane, ethane, propane, butane, pentane, ethylene, propylene, butene, butadiene, acetylene, and methylacetylene; ...</p> <p>In particular, the plasma polymer film consisting substantially of carbon and hydrogen alone constitutes a dense, pinhole-free, hard film on the substrate surface. It is preferred as a protective coating because of good wear resistance and the ability of maintaining outstanding stability for long time. (‘543 Patent at 3:23-36.)</p> <p>The energy density suitable for forming a plasma polymer film as a protective coating according to the present invention, $W/(FM)$, where W is the electric power for producing the plasma in J/sec, F is the feed gas flow rate in kg/sec, and M is the molecular weight of the feed gas, is at least 10^9 J/kg. The energy density for forming an anchor layer ranges from 10^7 to 10^9 J/kg. Hydrogen or other inert gas may be used as a carrier gas. Thus, when the feed gas consists substantially of carbon and hydrogen alone, except for some inevitable impurity gas present, the resulting plasma polymer film will exhibit high wear resistance and good adhesion to the base metal. (‘543 Patent at 4:18-31.)</p> <p>Next, a hydrocarbon polymer film was formed as a protective coating on the substrate surface under the conditions of pressure 0.02 Torr, RF power 500 W, and CH_4 5 SCCM. (‘543 Patent at 4:49-52.)</p> <p>A diamond-like film suited for use in the present invention can be formed in a variety of ways, preferably by ionization evaporation. The term diamond-like as used herein means "like diamond", that is, having a crystal structure in which each atom is the center of a tetrahedron formed by its nearest neighbors. Diamond-like film exhibits a diamond structure when measured, for example, by X-ray defraction analysis. The preferred technique consists of introducing a hydrocarbon feed gas or a feed gas capable of producing a hydrocarbon upon decomposition or reaction into a vacuum, ionizing the gas, and guiding the ionized gas and depositing</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
	<p>it on the metallic surface portion of a sliding member that constitutes a substrate to form a diamond-like thin film thereon. (‘543 Patent at 5:13-28.)</p> <p>As briefly described above, the present invention is characterized in forming a diamond-like film on the surface of sliding members of recording-playback devices. The film forming is preferably by ionization evaporation that produces a diamond-like film.</p> <p>Ionization evaporation is a process in which a hydrocarbon feed gas or a feed gas capable of producing a hydrocarbon upon decomposition or reaction ... is ionized by such ionizing means as arc discharge between a cathode and an anticathode or by thermionic emission between cathode hot filaments and an anticathode, and the resulting ion beam is accelerated by an electric field and directed to the substrate, whereby a diamond-like film is formed on the substrate.</p> <p>The ionization evaporation that forms a technical basis of the present invention is described in U.S. patent application Nos. 59377/1988, 59376/1988, etc. Working examples of the present invention use a process and an apparatus based on the equipment described in these prior publications. (‘543 Patent at 5:33 – 6:8.)</p> <p>The process of film forming will now be explained in detail with reference to FIG. 2 First, the chamber 31 is evacuated to a high vacuum of 10^{-6} Torr. A valve on the gas feed line 37 is manipulated to introduce methane gas or its mixture with hydrogen, with or without a carrier gas such as Ar, He, or Ne, at a predetermined flow rate via the inlet 35 into the chamber, while a desired gas pressure, e.g., 10^{-1} Torr, is maintained through control of the evacuation system 38. Meanwhile the plurality of hot cathode filaments 34 are heated with an alternating current I_f, and a potential difference V_d is applied across the filaments 34 and the anticathode 36 for an electric discharge. The methane gas from the feed inlet 35 is thermally decomposed and collides with the thermions from the filaments to generate positive ions and electrons. The electrons, in turn, collide with other thermally decomposed particles. The phenomenon is repeated under the containment action of the magnetic field</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")																																																																																					
	<p>of the solenoid until the methane gas is completely converted to positive ions of the thermally decomposed substance.</p> <p>The positive ions are attracted by the negative potential V_a applied to the electrode 32 and the grid 36. They are accelerated toward the slowly moving substrate S and impinge upon it to effect a film-forming reaction, whereby a diamond-like thin film is formed. (‘543 Patent at 6:36-61.)</p> <p>Using the hub of Comparative Example 1, the substrate was charged into the film-forming apparatus shown in FIG. 2. The vacuum chamber 10 was evacuated to 10^{-6} Torr, and then methane gas was introduced. At a gas pressure of 10^{-1} Torr, hot cathode filaments were allowed to cause an electric discharge. The magnetic flux density of the solenoid 39 was 400 gauss, the substrate voltage $V_a=200$ V, $V_d=30$ V, and the substrate temperature 200° C. An alternating current I_f of 25 A was flown through the filaments 34.</p> <p>The filaments were in the form of coils 3 mm wide surrounded by an electrode with a spacing of 8 mm in between, and the feed rate was 40 mm/hr.</p> <p>Next, V_a was changed to 450 V (the other conditions being left unchanged) and a diamond-like protective coating was made (Example 2). (‘543 Patent at 7:11-26.)</p> <div><p style="text-align: center;">TABLE 1</p><table><tr><th colspan="2"></th><th colspan="4">Protective coating</th><th colspan="4">Anchor layer</th></tr><tr><th colspan="2"></th><th>Film formed by</th><th>Material</th><th>Hardness</th><th>Film (μm) thickness</th><th>Film formed by</th><th>Material</th><th>Hardness</th><th>Film (μm) thickness</th></tr><tr><td>Comp. Ex. 1</td><td>Untreated</td><td></td><td>Stainless steel</td><td>200</td><td>—</td><td></td><td></td><td></td><td></td></tr><tr><td>Ex. 1</td><td>Anchored</td><td>Plasma</td><td>CH_4</td><td>2000</td><td>0.1</td><td>Plasma</td><td>CH_4</td><td>700</td><td>0.1</td></tr><tr><td>2</td><td>"</td><td>DLC</td><td>CH_4/H_2</td><td>5000</td><td>1.0</td><td>DLC</td><td>CH_4/H_2</td><td>2500</td><td>0.5</td></tr></table><p style="text-align: center;">TABLE 2</p><table><tr><th colspan="2"></th><th colspan="5">Stress test</th></tr><tr><th colspan="2"></th><th>Fric-tion (g · cm)</th><th>Wear resistance (μm)</th><th>Abrasion test</th><th>No. of metal particles peeled off (pc/mm²)</th><th>No. of defects (pc)</th></tr><tr><td>Comp. Ex. 1</td><td></td><td>9.5</td><td>1.0</td><td>15.0</td><td>1000</td><td>15</td></tr><tr><td>Ex. 1</td><td></td><td>9.0</td><td>0.2</td><td>1.0</td><td>100</td><td>5</td></tr><tr><td>2</td><td></td><td>7.0</td><td>≈ 0</td><td>≈ 0</td><td>0</td><td>0</td></tr></table></div> <p>[A] protective coating formed on the anchor layer, said protective coating consisting of a film selected from the</p>			Protective coating				Anchor layer						Film formed by	Material	Hardness	Film (μm) thickness	Film formed by	Material	Hardness	Film (μm) thickness	Comp. Ex. 1	Untreated		Stainless steel	200	—					Ex. 1	Anchored	Plasma	CH_4	2000	0.1	Plasma	CH_4	700	0.1	2	"	DLC	CH_4/H_2	5000	1.0	DLC	CH_4/H_2	2500	0.5			Stress test							Fric-tion (g · cm)	Wear resistance (μm)	Abrasion test	No. of metal particles peeled off (pc/mm ²)	No. of defects (pc)	Comp. Ex. 1		9.5	1.0	15.0	1000	15	Ex. 1		9.0	0.2	1.0	100	5	2		7.0	≈ 0	≈ 0	0	0
		Protective coating				Anchor layer																																																																																
		Film formed by	Material	Hardness	Film (μm) thickness	Film formed by	Material	Hardness	Film (μm) thickness																																																																													
Comp. Ex. 1	Untreated		Stainless steel	200	—																																																																																	
Ex. 1	Anchored	Plasma	CH_4	2000	0.1	Plasma	CH_4	700	0.1																																																																													
2	"	DLC	CH_4/H_2	5000	1.0	DLC	CH_4/H_2	2500	0.5																																																																													
		Stress test																																																																																				
		Fric-tion (g · cm)	Wear resistance (μm)	Abrasion test	No. of metal particles peeled off (pc/mm ²)	No. of defects (pc)																																																																																
Comp. Ex. 1		9.5	1.0	15.0	1000	15																																																																																
Ex. 1		9.0	0.2	1.0	100	5																																																																																
2		7.0	≈ 0	≈ 0	0	0																																																																																

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
	<p>group of</p> <p>(a') hydrocarbon plasma polymer film consisting of carbon and hydrogen and having an H/C value of about 1.5, the H/C value of the plasma polymer film of the protective coating being less than that of the anchor layer when the anchor layer consists of (a), said hydrocarbon plasma polymer film having a thickness in the range of about 100 Å to about 5000 Å, and</p> <p>(b') a diamond film formed by ionization evaporation having a Vickers hardness of at least about 5,000 kg/mm² when the anchor layer consists of (b), said diamond film having a thickness in the range of about 100 Å to about 1000 Å. ('543 Patent, Claim 1)</p>
<u>Claim 26</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p>[A] protective coating formed on the anchor layer, said protective coating consisting of a film selected from the group of</p> <p>(a') hydrocarbon plasma polymer film consisting of carbon and hydrogen and having an H/C value of about 1.5, the H/C value of the plasma polymer film of the protective coating being less than that of the anchor layer when the anchor layer consists of (a), said hydrocarbon plasma polymer film having a thickness in the range of about 100 Å to about 5000 Å, and</p> <p>(b') a diamond film formed by ionization evaporation having a Vickers hardness of at least about 5,000 kg/mm² when the anchor layer consists of (b), said diamond film having a thickness in the range of about 100 Å to about 1000 Å. ('543 Patent, Claim 1)</p>
<u>Claim 27</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.</p>	<p>[A] protective coating formed on the anchor layer, said protective coating consisting of a film selected from the group of</p> <p>(a') hydrocarbon plasma polymer film consisting of carbon and hydrogen and having an H/C value of about 1.5, the H/C value of the plasma polymer film of the protective coating being less than that of the anchor layer when the anchor layer</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
	<p>consists of (a), said hydrocarbon plasma polymer film having a thickness in the range of about 100 Å to about 5000 Å, and</p> <p>(b') a diamond film formed by ionization evaporation having a Vickers hardness of at least about 5,000 kg/mm² when the anchor layer consists of (b), said diamond film having a thickness in the range of about 100 Å to about 1000 Å.</p> <p>('543 Patent, Claim 1)</p>
<u>Claim 28</u>	
<p>The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.</p>	<p>A protectively coated sliding member comprises a sliding member body, an anchor layer formed thereon and which consists of (a) a hydrocarbon or hydrocarbon-based plasma polymer film, (b) a diamond-like film, or (c) an ion-plating film of a metal or metallic compound, and a protective coating formed on the anchor layer and which consists of a hydrocarbon or hydrocarbon-based plasma polymer film in case where the anchor layer consists of (a), a diamond or diamond-like film in case of (b), or an ion-plating film of a metallic compound in case of (c). The protective coating is of greater hardness than the anchor layer.</p> <p>('543 Patent at Abstract.)</p> <p>The present invention is characterized in that an anchor layer consisting of a plasma polymer film of a hydrocarbon or hydrocarbon-based monomer, a diamond-like film, or an ion plating film of a metal or metallic compound, and a protective coating consisting of a plasma polymer film of a hydrocarbon or hydrocarbon-based monomer of the same type as used in the anchor layer, a diamond or diamond-like film, or an ion plating film of a metallic compound, the protective coating being greater in hardness than the anchor layer, are provided on the surface of sliding members.</p> <p>...</p> <p>When the protective coating is a diamond or diamond-like film, the anchor layer is formed under a set of conditions so chosen as to give a diamond-like film of lower density than the protective coating.</p> <p>('543 Patent at 2:33-53.)</p> <p>A diamond-like film suited for use in the present invention can be formed in a variety of ways, preferably by ionization evaporation. The term diamond-like as used herein means</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
	<p>"like diamond", that is, having a crystal structure in which each atom is the center of a tetrahedron formed by its nearest neighbors. Diamond-like film exhibits a diamond structure when measured, for example, by X-ray defraction analysis. The preferred technique consists of introducing a hydrocarbon feed gas or a feed gas capable of producing a hydrocarbon upon decomposition or reaction into a vacuum, ionizing the gas, and guiding the ionized gas and depositing it on the metallic surface portion of a sliding member that constitutes a substrate to form a diamond-like thin film thereon. (‘543 Patent at 5:13-28.)</p> <p>As briefly described above, the present invention is characterized in forming a diamond-like film on the surface of sliding members of recording-playback devices. The film forming is preferably by ionization evaporation that produces a diamond-like film.</p> <p>Ionization evaporation is a process in which a hydrocarbon feed gas or a feed gas capable of producing a hydrocarbon upon decomposition or reaction ... is ionized by such ionizing means as arc discharge between a cathode and an anticathode or by thermionic emission between cathode hot filaments and an anticathode, and the resulting ion beam is accelerated by an electric field and directed to the substrate, whereby a diamond-like film is formed on the substrate.</p> <p>....</p> <p>The ionization evaporation that forms a technical basis of the present invention is described in U.S. patent application Nos. 59377/1988, 59376/1988, etc. Working examples of the present invention use a process and an apparatus based on the equipment described in these prior publications. (‘543 Patent at 5:33 – 6:8.)</p> <p>The process of film forming will now be explained in detail with reference to FIG. 2 First, the chamber 31 is evacuated to a high vacuum of 10^{-6} Torr. A valve on the gas feed line 37 is manipulated to introduce methane gas or its mixture with hydrogen, with or without a carrier gas such as Ar, He, or Ne, at a predetermined flow rate via the inlet 35 into the chamber, while a desired gas pressure, e.g., 10^{-1} Torr, is maintained through control of the evacuation system 38. Meanwhile the plurality of hot cathode filaments 34 are</p>

'086 Patent	U.S. Patent No. 5,288,543 ("543 Patent")
	<p>heated with an alternating current I_f, and a potential difference V_d is applied across the filaments 34 and the anticathode 36 for an electric discharge. The methane gas from the feed inlet 35 is thermally decomposed and collides with the thermions from the filaments to generate positive ions and electrons. The electrons, in turn, collide with other thermally decomposed particles. The phenomenon is repeated under the containment action of the magnetic field of the solenoid until the methane gas is completely converted to positive ions of the thermally decomposed substance.</p> <p>The positive ions are attracted by the negative potential V_a applied to the electrode 32 and the grid 36. They are accelerated toward the slowly moving substrate S and impinge upon it to effect a film-forming reaction, whereby a diamond-like thin film is formed. (‘543 Patent at 6:36-61.)</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The original parent application that eventually led to U.S. Patent No. 5,431,963 was filed on February 1, 1993, before the U.S. filing date of the '086 patent, or the filing dates of the Japanese applications to which the '086 patent claims priority.</p> <p>Elements below show a hard-carbon-film coated substrate.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>Accordingly, methods for depositing DLC films onto, for example, smooth aluminum electrodes and for fabricating field-graded electrodes prior to, for example, the deposition of DLC films thereon would be well received by the electrical industries. (963 Patent at 2:24-28)</p> <p>The present invention provides for PECVD of a DLC film onto a substrate. In one embodiment, a substrate is subjected to the following steps without interruption:</p> <p>plasma etching (e.g., with an argon plasma in the case of aluminum or a hydrogen plasma in the case of silicon) while maintaining said substrate at a temperature in the range of about 25°-100 °C. and negatively biasing it at a first preselected voltage;</p> <p>passing a first gaseous mixture comprising at least one hydrocarbon, usually methane, and argon through an electrical discharge to at least partially ionize the hydrocarbons to form DLC film on the substrate, while negatively biasing said substrate within a second preselected voltage range with an absolute value lower than that of said first preselected voltage; and</p> <p>passing a second gaseous mixture comprising at least one hydrocarbon and argon through said electrical discharge to at least partially ionize said hydrocarbons to form a second portion of said DLC film on said substrate.</p> <p>In another embodiment, the substrate is etched with a suitable plasma, maintained at a preselected DLC forming temperature and negatively biased as previously described. Said first gaseous mixture is partially ionized to form DLC film on the substrate. A second gaseous mixture of at least</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p>one hydrocarbon and hydrogen is then passed through the electrical discharge to at least partially ionize the hydrocarbons and form additional DLC film on the substrate. ('963 Patent at 2:58 – 3:20)</p> <p>The adhesion of DLC deposited by PECVD to, for example, smooth substrates such as aluminum may be improved, however, by modifying the conventional PECVD process to include a short but relatively high power CH₄ /Ar deposition step. The following comparative example is illustrative of the improvements in DLC adhesion to substrates which can be realized by modifying the conventional PECVD process in accordance with the precepts of the present invention.</p> <p>EXAMPLE 1</p> <p>DLC films of up to 10 microns were deposited onto silicon wafers coated with 1000 Å thick aluminum sputtered from a Perkin Elmer 4450 Delta Target Magnetron sputtering system and etched in an argon plasma in a Plasma Therm PK1241 Reactive Ion Etcher (RIE) system operated at an RF frequency of 13.56 MHz. The depositions were conducted using the powered electrode of said RIE system. The substrate was powered at from 60 to 250 watts depending upon the process steps employed, i.e., etching, high power argon deposition, or deposition, causing a varying negative bias voltage therein. A process gas stream consisting of methane and argon or hydrogen was introduced into the chamber of the Plasma Therm at preselected flow rates and a pressure of 0.5 Torr. The process conditions for two inventive deposition processes and each process step thereof are summarized in Tables 1-2.</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")																																																																												
	<p style="text-align: center;">TABLE 1</p> <hr/> <p style="text-align: center;">Deposition Temperature 100° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., the pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 were met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the flow of H₂ was increased and flow of Ar was simultaneously decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄H₂ Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>H₂:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-260 Volts</td></tr> <tr><td>Deposition Rate:</td><td>200 Å/min</td></tr> </table> <hr/> <p>The process was continued until the desired film thickness was obtained; e.g., 50 min. for a 10,000 Å thick film.</p> <p style="text-align: center;">TABLE 2</p> <hr/> <p style="text-align: center;">Deposition Temperature 37° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 are met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar High Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the power and bias were decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄/Ar Low Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>60 Watts</td></tr> <tr><td>Bias</td><td>-75 Volts</td></tr> <tr><td>Deposition Rate:</td><td>100 Å/min</td></tr> </table> <hr/> <p>The process was continued until the desired film thickness was obtained; e.g., 100 min. for a 10,000Å thick film. (963 Patent at 4:8 – 5:29)</p>	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		H ₂ :	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-260 Volts	Deposition Rate:	200 Å/min	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	60 Watts	Bias	-75 Volts	Deposition Rate:	100 Å/min
Flow Rate Ar:	100 sccm																																																																												
Pressure:	0.2 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-315 Volts																																																																												
Time	11 min																																																																												
<u>Flow Rate</u>																																																																													
Ar:	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-240 Volts																																																																												
Time	5 min																																																																												
<u>Flow Rate</u>																																																																													
H ₂ :	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-260 Volts																																																																												
Deposition Rate:	200 Å/min																																																																												
Flow Rate Ar:	100 sccm																																																																												
Pressure:	0.2 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-315 Volts																																																																												
Time	11 min																																																																												
<u>Flow Rate</u>																																																																													
Ar:	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-240 Volts																																																																												
Time	5 min																																																																												
<u>Flow Rate</u>																																																																													
Ar:	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	60 Watts																																																																												
Bias	-75 Volts																																																																												
Deposition Rate:	100 Å/min																																																																												

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p>[T]he samples fabricated under the inventive conditions summarized in Tables 1 and 2, which included a short, high-power Ar interfacial deposition step, showed good adhesion, i.e., no spalling, of the DLC film to the aluminum even at thicknesses as high as 10 μm. It is preferred that the process not be interrupted after the substrate has been etched. Depending upon design considerations, the process variables, i.e., gas composition, substrate bias, power, deposition time, etc., may be changed either stepwise or continuously to achieve special effects. (963 Patent at 5:34-44)</p> <p>Moreover, although the improvement in DLC film adherence has been illustrated in connection with relatively thick, e.g., 10 μm, DLC films and relatively smooth aluminum substrates (963 Patent at 5:52-56)</p> <p>3. The method of claim 1 wherein the substrate comprises aluminum. (963 Patent, Claim 3)</p> <p>6. The method of claim 4 wherein the substrate comprises aluminum. (963 Patent, Claim 6)</p>
<p>an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and</p>	<p>A diamondlike carbon (DLC) film is deposited by plasma enhanced chemical vapor deposition onto a substrate. A substrate is maintained at a preselected DLC forming temperature and is negatively biased at a first preselected voltage. A first gaseous mixture of hydrocarbons and argon is then passed through an electrical discharge to at least partially ionize the hydrocarbons to form DLC film on the substrate. (963 Patent at Abstract)</p> <p>The present invention is directed to the fabrication of field-graded electrodes and to the deposition of DLC films onto electrodes and other such substrates. By modifying the conventional PECVD process to include a short but relatively high power deposition step, the adhesion of thick DLC films to, for example, smooth electrode substrates may be improved.</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p data-bbox="646 275 951 306">('963 Patent at 2:31-37)</p> <p data-bbox="646 348 1419 453">The present invention provides for PECVD of a DLC film onto a substrate. In one embodiment, a substrate is subjected to the following steps without interruption:</p> <p data-bbox="646 495 1419 674">plasma etching (e.g., with an argon plasma in the case of aluminum or a hydrogen plasma in the case of silicon) while maintaining said substrate at a temperature in the range of about 25°-100 °C. and negatively biasing it at a first preselected voltage;</p> <p data-bbox="646 716 1419 968">passing a first gaseous mixture comprising at least one hydrocarbon, usually methane, and argon through an electrical discharge to at least partially ionize the hydrocarbons to form DLC film on the substrate, while negatively biasing said substrate within a second preselected voltage range with an absolute value lower than that of said first preselected voltage; and</p> <p data-bbox="646 1010 1419 1146">passing a second gaseous mixture comprising at least one hydrocarbon and argon through said electrical discharge to at least partially ionize said hydrocarbons to form a second portion of said DLC film on said substrate.</p> <p data-bbox="646 1188 1419 1503">In another embodiment, the substrate is etched with a suitable plasma, maintained at a preselected DLC forming temperature and negatively biased as previously described. Said first gaseous mixture is partially ionized to form DLC film on the substrate. A second gaseous mixture of at least one hydrocarbon and hydrogen is then passed through the electrical discharge to at least partially ionize the hydrocarbons and form additional DLC film on the substrate. ('963 Patent at 2:58 – 3:20)</p> <p data-bbox="646 1545 1419 1839">The adhesion of DLC deposited by PECVD to, for example, smooth substrates such as aluminum may be improved, however, by modifying the conventional PECVD process to include a short but relatively high power CH₄ /Ar deposition step. The following comparative example is illustrative of the improvements in DLC adhesion to substrates which can be realized by modifying the conventional PECVD process in accordance with the precepts of the present invention.</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")																																						
	<p data-bbox="646 270 818 300">EXAMPLE 1</p> <p data-bbox="646 344 1422 919">DLC films of up to 10 microns were deposited onto silicon wafers coated with 1000 Å thick aluminum sputtered from a Perkin Elmer 4450 Delta Target Magnetron sputtering system and etched in an argon plasma in a Plasma Therm PK1241 Reactive Ion Etcher (RIE) system operated at an RF frequency of 13.56 MHz. The depositions were conducted using the powered electrode of said RIE system. The substrate was powered at from 60 to 250 watts depending upon the process steps employed, i.e., etching, high power argon deposition, or deposition, causing a varying negative bias voltage therein. A process gas stream consisting of methane and argon or hydrogen was introduced into the chamber of the Plasma Therm at preselected flow rates and a pressure of 0.5 Torr. The process conditions for two inventive deposition processes and each process step thereof are summarized in Tables 1-2.</p> <div data-bbox="748 936 1328 1642"> <p data-bbox="984 940 1089 966" style="text-align: center;">TABLE 1</p> <hr/> <p data-bbox="906 976 1167 999" style="text-align: center;">Deposition Temperature 100° C.</p> <hr/> <p data-bbox="954 1010 1118 1033" style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table data-bbox="824 1037 1227 1155"> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p data-bbox="751 1163 1325 1203">After 11 min., the pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 were met.</p> <p data-bbox="922 1205 1159 1228" style="text-align: center;"><u>Step 2: CH₄/Ar Deposition</u></p> <table data-bbox="824 1232 1227 1396"> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p data-bbox="751 1407 1325 1446">After 5 min., the flow of H₂ was increased and flow of Ar was simultaneously decreased until the conditions of Step 3 were met.</p> <p data-bbox="927 1449 1154 1472" style="text-align: center;"><u>Step 3: CH₄H₂ Deposition</u></p> <table data-bbox="824 1476 1227 1640"> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>H₂:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-260 Volts</td></tr> <tr><td>Deposition Rate:</td><td>200 Å/min</td></tr> </table> <hr/> </div> <p data-bbox="646 1694 1390 1759">The process was continued until the desired film thickness was obtained; e.g., 50 min. for a 10,000 Å thick film.</p>	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		H ₂ :	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-260 Volts	Deposition Rate:	200 Å/min
Flow Rate Ar:	100 sccm																																						
Pressure:	0.2 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-315 Volts																																						
Time	11 min																																						
<u>Flow Rate</u>																																							
Ar:	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-240 Volts																																						
Time	5 min																																						
<u>Flow Rate</u>																																							
H ₂ :	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-260 Volts																																						
Deposition Rate:	200 Å/min																																						

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")																																						
	<p style="text-align: center;">TABLE 2</p> <hr/> <p style="text-align: center;">Deposition Temperature 37° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr> <td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr> <td>Pressure:</td><td>0.2 Torr</td></tr> <tr> <td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr> <td>Bias</td><td>-315 Volts</td></tr> <tr> <td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 are met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar High Power Deposition</u></p> <table> <tr> <td colspan="2"><u>Flow Rate</u></td></tr> <tr> <td>Ar:</td><td>100 sccm</td></tr> <tr> <td>CH₄:</td><td>50 sccm</td></tr> <tr> <td>Pressure:</td><td>0.5 Torr</td></tr> <tr> <td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr> <td>Bias</td><td>-240 Volts</td></tr> <tr> <td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the power and bias were decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄/Ar Low Power Deposition</u></p> <table> <tr> <td colspan="2"><u>Flow Rate</u></td></tr> <tr> <td>Ar:</td><td>100 sccm</td></tr> <tr> <td>CH₄:</td><td>50 sccm</td></tr> <tr> <td>Pressure:</td><td>0.5 Torr</td></tr> <tr> <td>Power @ 13.56 MHz:</td><td>60 Watts</td></tr> <tr> <td>Bias</td><td>-75 Volts</td></tr> <tr> <td>Deposition Rate:</td><td>100 Å/min</td></tr> </table> <hr/> <p>The process was continued until the desired film thickness was obtained; e.g., 100 min. for a 10,000Å thick film. ('963 Patent at 4:8 – 5:29)</p> <p>[T]he samples fabricated under the inventive conditions summarized in Tables 1 and 2, which included a short, high-power Ar interfacial deposition step, showed good adhesion, i.e., no spalling, of the DLC film to the aluminum even at thicknesses as high as 10 µm. It is preferred that the process not be interrupted after the substrate has been etched. Depending upon design considerations, the process variables, i.e., gas composition, substrate bias, power, deposition time, etc., may be changed either stepwise or continuously to achieve special effects. ('963 Patent at 5:34-44)</p> <p>1. A method for the plasma enhanced chemical vapor deposition of a diamondlike carbon film onto a metal substrate comprising performing the following steps at a temperature in the range of about 25°-100° C., without interruption:</p> <p>(A) plasma etching said substrate with argon while negatively biasing said substrate at a first voltage;</p> <p>(B) introducing hydrocarbon at an increasing flow rate to</p>	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	60 Watts	Bias	-75 Volts	Deposition Rate:	100 Å/min
Flow Rate Ar:	100 sccm																																						
Pressure:	0.2 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-315 Volts																																						
Time	11 min																																						
<u>Flow Rate</u>																																							
Ar:	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-240 Volts																																						
Time	5 min																																						
<u>Flow Rate</u>																																							
Ar:	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	60 Watts																																						
Bias	-75 Volts																																						
Deposition Rate:	100 Å/min																																						

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p>form a hydrocarbon-argon mixture and passing said mixture through an electrical discharge to at least partially ionize said hydrocarbon to form a first portion of said diamondlike carbon film on said substrate while negatively biasing said substrate at a second voltage with an absolute value lower than that of said first voltage; and</p> <p>(C) continuing passage of hydrocarbon and argon through said electrical discharge at a lower power and lower absolute bias value than in step B, to at least partially ionize said hydrocarbon to form a second portion of said diamondlike carbon film on said substrate. (963 Patent, Claim 1)</p> <p>4. A method for the plasma enhanced chemical vapor deposition of a diamondlike carbon film onto a metal substrate comprising performing the following steps at a temperature in the range of about 25°-100° C., without interruption:</p> <p>plasma etching said substrate with argon while negatively biasing said substrate;</p> <p>introducing hydrocarbon at an increasing flow rate to form a hydrocarbon-argon mixture and passing said mixture through an electrical discharge to at least partially ionize said hydrocarbon to form a first portion of said diamondlike carbon film on said substrate, and</p> <p>gradually decreasing the argon flow and introducing hydrogen at an increasing flow rate while continuing passage of the resulting mixture through said electrical discharge to at least partially ionize said hydrocarbon to form a second portion of said diamondlike carbon film on said substrate. (963 Patent, Claim 4)</p>
a hard carbon film arranged on said intermediate layer.	<p>The substrate is then negatively biased at a second preselected voltage lower than the first preselected voltage. A second gaseous mixture of hydrocarbons and argon or hydrogen is then passed through the electrical discharge to at least partially ionize the hydrocarbons to form additional DLC film on the substrate. (963 Patent at Abstract)</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p>DLC films are characterized by an amorphous, polymer-like hydrogen and carbon structure but exhibit physical properties similar to those of single-crystal diamond. (963 Patent at 1:36-39)</p> <p>The present invention provides for PECVD of a DLC film onto a substrate. In one embodiment, a substrate is subjected to the following steps without interruption:</p> <p>plasma etching (e.g., with an argon plasma in the case of aluminum or a hydrogen plasma in the case of silicon) while maintaining said substrate at a temperature in the range of about 25°-100 °C. and negatively biasing it at a first preselected voltage;</p> <p>passing a first gaseous mixture comprising at least one hydrocarbon, usually methane, and argon through an electrical discharge to at least partially ionize the hydrocarbons to form DLC film on the substrate, while negatively biasing said substrate within a second preselected voltage range with an absolute value lower than that of said first preselected voltage; and</p> <p>passing a second gaseous mixture comprising at least one hydrocarbon and argon through said electrical discharge to at least partially ionize said hydrocarbons to form a second portion of said DLC film on said substrate.</p> <p>In another embodiment, the substrate is etched with a suitable plasma, maintained at a preselected DLC forming temperature and negatively biased as previously described. Said first gaseous mixture is partially ionized to form DLC film on the substrate. A second gaseous mixture of at least one hydrocarbon and hydrogen is then passed through the electrical discharge to at least partially ionize the hydrocarbons and form additional DLC film on the substrate. (963 Patent at 2:58 – 3:20)</p> <p>Conventional processes for the low-pressure, metastable growth of DLC films including plasma enhanced (PECVD) techniques are disclosed in, for example, Angus et al., "Low-Pressure Metastable Growth of Diamond and `Diamondlike` Phases", Science, vol. 241, pages 913-921 (Aug. 19, 1988), incorporated herein by reference.</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p data-bbox="646 268 950 302">('963 Patent at 3:35-41)</p> <p data-bbox="646 344 1421 632">The adhesion of DLC deposited by PECVD to, for example, smooth substrates such as aluminum may be improved, however, by modifying the conventional PECVD process to include a short but relatively high power CH₄ /Ar deposition step. The following comparative example is illustrative of the improvements in DLC adhesion to substrates which can be realized by modifying the conventional PECVD process in accordance with the precepts of the present invention.</p> <p data-bbox="646 674 818 703">EXAMPLE 1</p> <p data-bbox="646 745 1421 1320">DLC films of up to 10 microns were deposited onto silicon wafers coated with 1000 Å thick aluminum sputtered from a Perkin Elmer 4450 Delta Target Magnetron sputtering system and etched in an argon plasma in a Plasma Therm PK1241 Reactive Ion Etcher (RIE) system operated at an RF frequency of 13.56 MHz. The depositions were conducted using the powered electrode of said RIE system. The substrate was powered at from 60 to 250 watts depending upon the process steps employed, i.e., etching, high power argon deposition, or deposition, causing a varying negative bias voltage therein. A process gas stream consisting of methane and argon or hydrogen was introduced into the chamber of the Plasma Therm at preselected flow rates and a pressure of 0.5 Torr. The process conditions for two inventive deposition processes and each process step thereof are summarized in Tables 1-2.</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")																																																																												
	<p style="text-align: center;">TABLE 1</p> <hr/> <p style="text-align: center;">Deposition Temperature 100° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., the pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 were met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the flow of H₂ was increased and flow of Ar was simultaneously decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄H₂ Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>H₂:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-260 Volts</td></tr> <tr><td>Deposition Rate:</td><td>200 Å/min</td></tr> </table> <hr/> <p>The process was continued until the desired film thickness was obtained; e.g., 50 min. for a 10,000 Å thick film.</p> <p style="text-align: center;">TABLE 2</p> <hr/> <p style="text-align: center;">Deposition Temperature 37° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 are met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar High Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the power and bias were decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄/Ar Low Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>60 Watts</td></tr> <tr><td>Bias</td><td>-75 Volts</td></tr> <tr><td>Deposition Rate:</td><td>100 Å/min</td></tr> </table> <hr/> <p>The process was continued until the desired film thickness was obtained; e.g., 100 min. for a 10,000Å thick film. ('963 Patent at 4:8 – 5:29)</p>	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		H ₂ :	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-260 Volts	Deposition Rate:	200 Å/min	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	60 Watts	Bias	-75 Volts	Deposition Rate:	100 Å/min
Flow Rate Ar:	100 sccm																																																																												
Pressure:	0.2 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-315 Volts																																																																												
Time	11 min																																																																												
<u>Flow Rate</u>																																																																													
Ar:	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-240 Volts																																																																												
Time	5 min																																																																												
<u>Flow Rate</u>																																																																													
H ₂ :	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-260 Volts																																																																												
Deposition Rate:	200 Å/min																																																																												
Flow Rate Ar:	100 sccm																																																																												
Pressure:	0.2 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-315 Volts																																																																												
Time	11 min																																																																												
<u>Flow Rate</u>																																																																													
Ar:	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-240 Volts																																																																												
Time	5 min																																																																												
<u>Flow Rate</u>																																																																													
Ar:	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	60 Watts																																																																												
Bias	-75 Volts																																																																												
Deposition Rate:	100 Å/min																																																																												

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p>[T]he samples fabricated under the inventive conditions summarized in Tables 1 and 2, which included a short, high-power Ar interfacial deposition step, showed good adhesion, i.e., no spalling, of the DLC film to the aluminum even at thicknesses as high as 10 μm. It is preferred that the process not be interrupted after the substrate has been etched. Depending upon design considerations, the process variables, i.e., gas composition, substrate bias, power, deposition time, etc., may be changed either stepwise or continuously to achieve special effects. (963 Patent at 5:34-44)</p> <p>1. A method for the plasma enhanced chemical vapor deposition of a diamondlike carbon film onto a metal substrate comprising performing the following steps at a temperature in the range of about 25°-100° C., without interruption:</p> <p>(A) plasma etching said substrate with argon while negatively biasing said substrate at a first voltage;</p> <p>(B) introducing hydrocarbon at an increasing flow rate to form a hydrocarbon-argon mixture and passing said mixture through an electrical discharge to at least partially ionize said hydrocarbon to form a first portion of said diamondlike carbon film on said substrate while negatively biasing said substrate at a second voltage with an absolute value lower than that of said first voltage; and</p> <p>(C) continuing passage of hydrocarbon and argon through said electrical discharge at a lower power and lower absolute bias value than in step B, to at least partially ionize said hydrocarbon to form a second portion of said diamondlike carbon film on said substrate. (963 Patent, Claim 1)</p> <p>4. A method for the plasma enhanced chemical vapor deposition of a diamondlike carbon film onto a metal substrate comprising performing the following steps at a temperature in the range of about 25°-100° C., without interruption:</p> <p>plasma etching said substrate with argon while negatively</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")																																														
	<p>biasing said substrate;</p> <p>introducing hydrocarbon at an increasing flow rate to form a hydrocarbon-argon mixture and passing said mixture through an electrical discharge to at least partially ionize said hydrocarbon to form a first portion of said diamondlike carbon film on said substrate, and</p> <p>gradually decreasing the argon flow and introducing hydrogen at an increasing flow rate while continuing passage of the resulting mixture through said electrical discharge to at least partially ionize said hydrocarbon to form a second portion of said diamondlike carbon film on said substrate. (963 Patent, Claim 4)</p>																																														
Claim 26																																															
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p style="text-align: center;">TABLE 1</p> <table border="1"> <thead> <tr> <th colspan="2">Deposition Temperature 100° C.</th> </tr> </thead> <tbody> <tr> <td colspan="2" style="text-align: center;"><u>Step 1: Plasma Etch</u></td> </tr> <tr> <td>Flow Rate Ar:</td> <td>100 sccm</td> </tr> <tr> <td>Pressure:</td> <td>0.2 Torr</td> </tr> <tr> <td>Power @ 13.56 MHz:</td> <td>250 Watts</td> </tr> <tr> <td>Bias</td> <td>-315 Volts</td> </tr> <tr> <td>Time</td> <td>11 min</td> </tr> </tbody> </table> <p>After 11 min., the pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 were met.</p> <table border="1"> <thead> <tr> <th colspan="2"><u>Step 2: CH₄/Ar Deposition</u></th> </tr> </thead> <tbody> <tr> <td colspan="2"><u>Flow Rate</u></td> </tr> <tr> <td>Ar:</td> <td>100 sccm</td> </tr> <tr> <td>CH₄:</td> <td>50 sccm</td> </tr> <tr> <td>Pressure:</td> <td>0.5 Torr</td> </tr> <tr> <td>Power @ 13.56 MHz:</td> <td>250 Watts</td> </tr> <tr> <td>Bias</td> <td>-240 Volts</td> </tr> <tr> <td>Time</td> <td>5 min</td> </tr> </tbody> </table> <p>After 5 min., the flow of H₂ was increased and flow of Ar was simultaneously decreased until the conditions of Step 3 were met.</p> <table border="1"> <thead> <tr> <th colspan="2"><u>Step 3: CH₄H₂ Deposition</u></th> </tr> </thead> <tbody> <tr> <td colspan="2"><u>Flow Rate</u></td> </tr> <tr> <td>H₂:</td> <td>100 sccm</td> </tr> <tr> <td>CH₄:</td> <td>50 sccm</td> </tr> <tr> <td>Pressure:</td> <td>0.5 Torr</td> </tr> <tr> <td>Power @ 13.56 MHz:</td> <td>250 Watts</td> </tr> <tr> <td>Bias</td> <td>-260 Volts</td> </tr> <tr> <td>Deposition Rate:</td> <td>200 Å/min</td> </tr> </tbody> </table> <p>The process was continued until the desired film thickness was obtained; e.g., 50 min. for a 10,000 Å thick film.</p>	Deposition Temperature 100° C.		<u>Step 1: Plasma Etch</u>		Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Step 2: CH₄/Ar Deposition</u>		<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Step 3: CH₄H₂ Deposition</u>		<u>Flow Rate</u>		H ₂ :	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-260 Volts	Deposition Rate:	200 Å/min
Deposition Temperature 100° C.																																															
<u>Step 1: Plasma Etch</u>																																															
Flow Rate Ar:	100 sccm																																														
Pressure:	0.2 Torr																																														
Power @ 13.56 MHz:	250 Watts																																														
Bias	-315 Volts																																														
Time	11 min																																														
<u>Step 2: CH₄/Ar Deposition</u>																																															
<u>Flow Rate</u>																																															
Ar:	100 sccm																																														
CH ₄ :	50 sccm																																														
Pressure:	0.5 Torr																																														
Power @ 13.56 MHz:	250 Watts																																														
Bias	-240 Volts																																														
Time	5 min																																														
<u>Step 3: CH₄H₂ Deposition</u>																																															
<u>Flow Rate</u>																																															
H ₂ :	100 sccm																																														
CH ₄ :	50 sccm																																														
Pressure:	0.5 Torr																																														
Power @ 13.56 MHz:	250 Watts																																														
Bias	-260 Volts																																														
Deposition Rate:	200 Å/min																																														

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")																																						
	<p style="text-align: center;">TABLE 2</p> <hr/> <p style="text-align: center;">Deposition Temperature 37° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 are met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar High Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the power and bias were decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄/Ar Low Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>60 Watts</td></tr> <tr><td>Bias</td><td>-75 Volts</td></tr> <tr><td>Deposition Rate:</td><td>100 Å/min</td></tr> </table> <hr/> <p>The process was continued until the desired film thickness was obtained; e.g., 100 min. for a 10,000Å thick film. (963 Patent at 4:38 – 5:29)</p>	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	60 Watts	Bias	-75 Volts	Deposition Rate:	100 Å/min
Flow Rate Ar:	100 sccm																																						
Pressure:	0.2 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-315 Volts																																						
Time	11 min																																						
<u>Flow Rate</u>																																							
Ar:	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-240 Volts																																						
Time	5 min																																						
<u>Flow Rate</u>																																							
Ar:	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	60 Watts																																						
Bias	-75 Volts																																						
Deposition Rate:	100 Å/min																																						
<u>Claim 27</u>																																							
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.</p>	<p style="text-align: center;">TABLE 1</p> <hr/> <p style="text-align: center;">Deposition Temperature 100° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., the pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 were met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the flow of H₂ was increased and flow of Ar was simultaneously decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄H₂ Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>H₂:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-260 Volts</td></tr> <tr><td>Deposition Rate:</td><td>200 Å/min</td></tr> </table> <hr/>	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		H ₂ :	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-260 Volts	Deposition Rate:	200 Å/min
Flow Rate Ar:	100 sccm																																						
Pressure:	0.2 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-315 Volts																																						
Time	11 min																																						
<u>Flow Rate</u>																																							
Ar:	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-240 Volts																																						
Time	5 min																																						
<u>Flow Rate</u>																																							
H ₂ :	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-260 Volts																																						
Deposition Rate:	200 Å/min																																						

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")																																						
	<p>The process was continued until the desired film thickness was obtained; e.g., 50 min. for a 10,000 Å thick film.</p> <p style="text-align: center;">TABLE 2</p> <hr/> <p style="text-align: center;">Deposition Temperature 37° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 are met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar High Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the power and bias were decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄/Ar Low Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>60 Watts</td></tr> <tr><td>Bias</td><td>-75 Volts</td></tr> <tr><td>Deposition Rate:</td><td>100 Å/min</td></tr> </table> <hr/> <p>The process was continued until the desired film thickness was obtained; e.g., 100 min. for a 10,000Å thick film. (963 Patent at 4:38 – 5:29)</p>	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	60 Watts	Bias	-75 Volts	Deposition Rate:	100 Å/min
Flow Rate Ar:	100 sccm																																						
Pressure:	0.2 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-315 Volts																																						
Time	11 min																																						
<u>Flow Rate</u>																																							
Ar:	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	250 Watts																																						
Bias	-240 Volts																																						
Time	5 min																																						
<u>Flow Rate</u>																																							
Ar:	100 sccm																																						
CH ₄ :	50 sccm																																						
Pressure:	0.5 Torr																																						
Power @ 13.56 MHz:	60 Watts																																						
Bias	-75 Volts																																						
Deposition Rate:	100 Å/min																																						
<u>Claim 28</u>																																							
<p>The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.</p>	<p>A diamondlike carbon (DLC) film is deposited by plasma enhanced chemical vapor deposition onto a substrate. A substrate is maintained at a preselected DLC forming temperature and is negatively biased at a first preselected voltage. A first gaseous mixture of hydrocarbons and argon is then passed through an electrical discharge to at least partially ionize the hydrocarbons to form DLC film on the substrate. The substrate is then negatively biased at a second preselected voltage lower than the first preselected voltage. A second gaseous mixture of hydrocarbons and argon or hydrogen is then passed through the electrical discharge to at least partially ionize the hydrocarbons to form additional DLC film on the substrate. (963 Patent at Abstract)</p> <p>DLC films are characterized by an amorphous, polymer-like hydrogen and carbon structure but exhibit physical properties similar to those of single-crystal diamond. (963 Patent at 1:36-39)</p>																																						

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p>The present invention provides for PECVD of a DLC film onto a substrate. In one embodiment, a substrate is subjected to the following steps without interruption:</p> <p>plasma etching (e.g., with an argon plasma in the case of aluminum or a hydrogen plasma in the case of silicon) while maintaining said substrate at a temperature in the range of about 25°-100 °C. and negatively biasing it at a first preselected voltage;</p> <p>passing a first gaseous mixture comprising at least one hydrocarbon, usually methane, and argon through an electrical discharge to at least partially ionize the hydrocarbons to form DLC film on the substrate, while negatively biasing said substrate within a second preselected voltage range with an absolute value lower than that of said first preselected voltage; and</p> <p>passing a second gaseous mixture comprising at least one hydrocarbon and argon through said electrical discharge to at least partially ionize said hydrocarbons to form a second portion of said DLC film on said substrate.</p> <p>In another embodiment, the substrate is etched with a suitable plasma, maintained at a preselected DLC forming temperature and negatively biased as previously described. Said first gaseous mixture is partially ionized to form DLC film on the substrate. A second gaseous mixture of at least one hydrocarbon and hydrogen is then passed through the electrical discharge to at least partially ionize the hydrocarbons and form additional DLC film on the substrate. ('963 Patent at 2:58 – 3:20)</p> <p>Conventional processes for the low-pressure, metastable growth of DLC films including plasma enhanced (PECVD) techniques are disclosed in, for example, Angus et al., "Low-Pressure Metastable Growth of Diamond and `Diamondlike` Phases", Science, vol. 241, pages 913-921 (Aug. 19, 1988), incorporated herein by reference. ('963 Patent at 3:35-41)</p> <p>The adhesion of DLC deposited by PECVD to, for example, smooth substrates such as aluminum may be improved,</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p>however, by modifying the conventional PECVD process to include a short but relatively high power CH₄ /Ar deposition step. The following comparative example is illustrative of the improvements in DLC adhesion to substrates which can be realized by modifying the conventional PECVD process in accordance with the precepts of the present invention.</p> <p>EXAMPLE 1</p> <p>DLC films of up to 10 microns were deposited onto silicon wafers coated with 1000 Å thick aluminum sputtered from a Perkin Elmer 4450 Delta Target Magnetron sputtering system and etched in an argon plasma in a Plasma Therm PK1241 Reactive Ion Etcher (RIE) system operated at an RF frequency of 13.56 MHz. The depositions were conducted using the powered electrode of said RIE system. The substrate was powered at from 60 to 250 watts depending upon the process steps employed, i.e., etching, high power argon deposition, or deposition, causing a varying negative bias voltage therein. A process gas stream consisting of methane and argon or hydrogen was introduced into the chamber of the Plasma Therm at preselected flow rates and a pressure of 0.5 Torr. The process conditions for two inventive deposition processes and each process step thereof are summarized in Tables 1-2.</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")																																																																												
	<p style="text-align: center;">TABLE 1</p> <hr/> <p style="text-align: center;">Deposition Temperature 100° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., the pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 were met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the flow of H₂ was increased and flow of Ar was simultaneously decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄H₂ Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>H₂:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-260 Volts</td></tr> <tr><td>Deposition Rate:</td><td>200 Å/min</td></tr> </table> <hr/> <p>The process was continued until the desired film thickness was obtained; e.g., 50 min. for a 10,000 Å thick film.</p> <p style="text-align: center;">TABLE 2</p> <hr/> <p style="text-align: center;">Deposition Temperature 37° C.</p> <hr/> <p style="text-align: center;"><u>Step 1: Plasma Etch</u></p> <table> <tr><td>Flow Rate Ar:</td><td>100 sccm</td></tr> <tr><td>Pressure:</td><td>0.2 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-315 Volts</td></tr> <tr><td>Time</td><td>11 min</td></tr> </table> <hr/> <p>After 11 min., pressure was increased to 0.5 Torr for 1 min. and other process conditions were changed gradually until the conditions of Step 2 are met.</p> <p style="text-align: center;"><u>Step 2: CH₄/Ar High Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>250 Watts</td></tr> <tr><td>Bias</td><td>-240 Volts</td></tr> <tr><td>Time</td><td>5 min</td></tr> </table> <hr/> <p>After 5 min., the power and bias were decreased until the conditions of Step 3 were met.</p> <p style="text-align: center;"><u>Step 3: CH₄/Ar Low Power Deposition</u></p> <table> <tr><td colspan="2"><u>Flow Rate</u></td></tr> <tr><td>Ar:</td><td>100 sccm</td></tr> <tr><td>CH₄:</td><td>50 sccm</td></tr> <tr><td>Pressure:</td><td>0.5 Torr</td></tr> <tr><td>Power @ 13.56 MHz:</td><td>60 Watts</td></tr> <tr><td>Bias</td><td>-75 Volts</td></tr> <tr><td>Deposition Rate:</td><td>100 Å/min</td></tr> </table> <hr/> <p>The process was continued until the desired film thickness was obtained; e.g., 100 min. for a 10,000Å thick film. (963 Patent at 4:8 – 5:29)</p>	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		H ₂ :	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-260 Volts	Deposition Rate:	200 Å/min	Flow Rate Ar:	100 sccm	Pressure:	0.2 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-315 Volts	Time	11 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	250 Watts	Bias	-240 Volts	Time	5 min	<u>Flow Rate</u>		Ar:	100 sccm	CH ₄ :	50 sccm	Pressure:	0.5 Torr	Power @ 13.56 MHz:	60 Watts	Bias	-75 Volts	Deposition Rate:	100 Å/min
Flow Rate Ar:	100 sccm																																																																												
Pressure:	0.2 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-315 Volts																																																																												
Time	11 min																																																																												
<u>Flow Rate</u>																																																																													
Ar:	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-240 Volts																																																																												
Time	5 min																																																																												
<u>Flow Rate</u>																																																																													
H ₂ :	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-260 Volts																																																																												
Deposition Rate:	200 Å/min																																																																												
Flow Rate Ar:	100 sccm																																																																												
Pressure:	0.2 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-315 Volts																																																																												
Time	11 min																																																																												
<u>Flow Rate</u>																																																																													
Ar:	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	250 Watts																																																																												
Bias	-240 Volts																																																																												
Time	5 min																																																																												
<u>Flow Rate</u>																																																																													
Ar:	100 sccm																																																																												
CH ₄ :	50 sccm																																																																												
Pressure:	0.5 Torr																																																																												
Power @ 13.56 MHz:	60 Watts																																																																												
Bias	-75 Volts																																																																												
Deposition Rate:	100 Å/min																																																																												

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p>[T]he samples fabricated under the inventive conditions summarized in Tables 1 and 2, which included a short, high-power Ar interfacial deposition step, showed good adhesion, i.e., no spalling, of the DLC film to the aluminum even at thicknesses as high as 10 μm. It is preferred that the process not be interrupted after the substrate has been etched. Depending upon design considerations, the process variables, i.e., gas composition, substrate bias, power, deposition time, etc., may be changed either stepwise or continuously to achieve special effects. (963 Patent at 5:34-44)</p> <p>1. A method for the plasma enhanced chemical vapor deposition of a diamondlike carbon film onto a metal substrate comprising performing the following steps at a temperature in the range of about 25°-100° C., without interruption:</p> <p>(A) plasma etching said substrate with argon while negatively biasing said substrate at a first voltage;</p> <p>(B) introducing hydrocarbon at an increasing flow rate to form a hydrocarbon-argon mixture and passing said mixture through an electrical discharge to at least partially ionize said hydrocarbon to form a first portion of said diamondlike carbon film on said substrate while negatively biasing said substrate at a second voltage with an absolute value lower than that of said first voltage; and</p> <p>(C) continuing passage of hydrocarbon and argon through said electrical discharge at a lower power and lower absolute bias value than in step B, to at least partially ionize said hydrocarbon to form a second portion of said diamondlike carbon film on said substrate. (963 Patent, Claim 1)</p> <p>4. A method for the plasma enhanced chemical vapor deposition of a diamondlike carbon film onto a metal substrate comprising performing the following steps at a temperature in the range of about 25°-100° C., without interruption:</p> <p>plasma etching said substrate with argon while negatively</p>

'086 Patent	U.S. Patent No. 5,431,963 ("963 Patent")
	<p>biasing said substrate;</p> <p>introducing hydrocarbon at an increasing flow rate to form a hydrocarbon-argon mixture and passing said mixture through an electrical discharge to at least partially ionize said hydrocarbon to form a first portion of said diamondlike carbon film on said substrate, and</p> <p>gradually decreasing the argon flow and introducing hydrogen at an increasing flow rate while continuing passage of the resulting mixture through said electrical discharge to at least partially ionize said hydrocarbon to form a second portion of said diamondlike carbon film on said substrate. (963 Patent, Claim 4)</p>

'086 Patent	Japanese Patent App. Pub. No. 63-286334 ("JP '334")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>Japanese Patent Application Publication No. 63-286334 was published on November 24, 1988, over one year before the U.S. filing date of the '086 patent.</p> <p>Elements below show hard carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>According to the present invention, as the substrate in contact with the exited gas ingredients may be made of the inorganic substances (such as glass, ceramics) and metals (such as titanium, silica, aluminum, tungsten and alloys containing these metals), or other substrate adopted in formation of the hard carbon film. In particular, according to the present invention, it is preferred the metal substrate made of the metal atoms contained in the primary gas be used.</p> <p>(JP '334, translation at p. 8).</p> <p>Examples of the primary gases include titanium compounds (such as titanium tetrachloride), silicon compounds (such as monosilane, disilane, trisilane, tetrasilane, pentasilane, methyl silane, dimethyl silane, trimethyl silane, tetramethyl silane, metal [sic, methyl] chlorosilane, phenyl chlorosilane, trimethyl silanol, triethyl silanol, triphenyl silanol, silicon tetrafluoride, silicon tetrachloride, silicon tetrabromide and silicon dioxide), aluminum compounds (such as aluminum trichloride, trimethyl aluminum)...</p> <p>(JP '334, translation at p. 5).</p>
an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and	<p>A laminate characterized in that it is prepared by laminating a substrate and a hard carbon film via an intermediate layer, which has a concentration gradient of the ingredients, that is, which has the content of the metal ingredient decreasing from the substrate towards the hard carbon film, and, at the same time, has the content of the ingredient for forming the hard carbon film increasing in said direction.</p> <p>(JP '334, translation at p. 1).</p> <p>the intermediate layer has a concentration gradient of the ingredients, that is, it has the content of the metal ingredient decreasing continuously, and it has the content of the ingredient for forming the hard carbon film increasing continuously.</p> <p>(JP '334, translation at p. 1).</p>

'086 Patent	Japanese Patent App. Pub. No. 63-286334 ("JP '334")
	<p>The laminate of the present invention is a laminate having a prescribed intermediate layer. By arranging a hard carbon film on the intermediate layer arranged on the substrate, it is possible to use the intermediate layer to relax the stress generated due to difference in the properties between the substrate and the hard carbon film. (JP '334, translation at p. 4).</p> <p>Examples of the secondary gases include hydrocarbon gases (such as methane, ethane), alcohols (such as methanol, ethanol), ketones (such as acetone, methyl ethyl ketone, diethyl ketone), alkyl amine (such as trimethylamine), and other compounds containing methyl groups as a portion of their structures; unsaturated hydrocarbon gases (such as ethylene), carbon monoxide, carbon dioxide, and other precursory compounds that can react with hydrogen atoms to generate the compounds containing methyl groups as a portion of their structures. These secondary gases may be used either alone or as a mixture of two or more types. In particular, according to the present invention, it is preferred that the secondary gas be selected from methane gas, acetone, methyl alcohol, and carbon monoxide. (JP '334, translation at p. 6).</p> <p>In this way, the feeding rates of the primary gas and the secondary gas are continuously increased/decreased, so that a continuous concentration gradient is formed for the contents of the metal ingredient and the hard carbon film forming ingredient in the intermediate layer.</p> <p>The primary gas and secondary gas fed into the reaction apparatus are in the gas phase, and, as energy of heat or microwave or the like is applied, they become the excited state. The gas ingredients in the excited state are brought in contact with the substrate so that they are deposited on the substrate to form an intermediate layer. The contents of the metal atoms and the carbon atoms in the intermediate layer formed in this way correspond to the molar ratio of the metal atoms and the carbon atoms in the primary gas and secondary gas, which are fed into the reaction apparatus with the feeding rates varying over time. (JP '334, translation at p. 8).</p> <p>By using such metal substrate, the metal substrate and the intermediate layer form a continuous layer.</p>

'086 Patent	Japanese Patent App. Pub. No. 63-286334 ("JP '334")
	(JP '334, translation at p. 8).
a hard carbon film arranged on said intermediate layer.	<p>the metal ingredient includes one type of atoms selected from the group comprising silicon atoms, titanium atoms, aluminum atoms, and tungsten atoms, and the ingredient forming the hard carbon film includes one type selected from the group comprising the diamond-state carbon and diamond. (JP '334, translation at p. 2).</p> <p>the hard carbon film is a type of film selected from the group comprising diamond-state carbon film and diamond film. (JP '334, translation at p. 2).</p> <p>The present invention relates to a laminate having a substrate and a hard carbon film, such as a diamond film or a diamond-state carbon film or the like, as well as a manufacturing method of the aforementioned laminate. More specifically, the present invention provides a laminate having a hard carbon film, which has excellent adhesive strength on the substrate, laminated on the substrate, and a novel method for manufacturing the laminate. (JP '334, translation at p. 3).</p> <p>The laminate of the present invention is a laminate having a prescribed intermediate layer. By arranging a hard carbon film on the intermediate layer arranged on the substrate, it is possible to use the intermediate layer to relax the stress generated due to difference in the properties between the substrate and the hard carbon film. (JP '334, translation at p. 4).</p> <p>By using such metal substrate, the metal substrate and the intermediate layer form a continuous layer. In addition, by adopting the aforementioned good method, a continuous layer is also formed for the intermediate layer and the hard carbon film. Consequently, in such case, a continuous layer is formed from the substrate to the hard carbon film. (JP '334, translation at p. 8).</p> <p>The reaction conditions for the hard carbon film forming region can be set according to the conditions when the hard carbon film is formed. Usually, the conditions are the same</p>

'086 Patent	Japanese Patent App. Pub. No. 63-286334 ("JP '334")
	<p>as the conditions when the intermediate layer is formed.</p> <p>The hard carbon film formed in this way may be either a diamond film or a diamond-state carbon film. (JP '334, translation at p. 9-10).</p>
<u>Claim 26</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.</p>	<p>the thickness of the intermediate layer is 0.01 μm or thicker. (JP '334, translation at p. 2).</p> <p>The thickness of the intermediate layer formed in this way usually is 0.01 μm or thicker (preferably 0.1 to 10 μm) (JP '334, translation at p. 9).</p> <p>The obtained laminate has a total thickness of the intermediate layer and the hard carbon film of 1 μm. Among the total thickness, the thickness of the intermediate layer is 0.1 μm, and the thickness of the hard carbon film is 0.9 μm. (JP '334, translation at p. 11).</p>
<u>Claim 27</u>	
<p>The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.</p>	<p>the thickness of the intermediate layer is 0.01 μm or thicker. (JP '334, translation at p. 2).</p> <p>The thickness of the intermediate layer formed in this way usually is 0.01 μm or thicker (preferably 0.1 to 10 μm) (JP '334, translation at p. 9).</p> <p>The obtained laminate has a total thickness of the intermediate layer and the hard carbon film of 1 μm. Among the total thickness, the thickness of the intermediate layer is 0.1 μm, and the thickness of the hard carbon film is 0.9 μm. (JP '334, translation at p. 11).</p>
<u>Claim 28</u>	
<p>The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.</p>	<p>the metal ingredient includes one type of atoms selected from the group comprising silicon atoms, titanium atoms, aluminum atoms, and tungsten atoms, and the ingredient forming the hard carbon film includes one type selected from the group comprising the diamond-state carbon and diamond. (JP '334, translation at p. 2).</p> <p>the hard carbon film is a type of film selected from the group comprising diamond-state carbon film and diamond film. (JP '334, translation at p. 2).</p>

'086 Patent	Japanese Patent App. Pub. No. 63-286334 ("JP '334")
	<p>The present invention relates to a laminate having a substrate and a hard carbon film, such as a diamond film or a diamond-state carbon film or the like, as well as a manufacturing method of the aforementioned laminate. More specifically, the present invention provides a laminate having a hard carbon film, which has excellent adhesive strength on the substrate, laminated on the substrate, and a novel method for manufacturing the laminate. (JP '334, translation at p. 3).</p> <p>The laminate of the present invention is a laminate having a prescribed intermediate layer. By arranging a hard carbon film on the intermediate layer arranged on the substrate, it is possible to use the intermediate layer to relax the stress generated due to difference in the properties between the substrate and the hard carbon film. (JP '334, translation at p. 4).</p> <p>By using such metal substrate, the metal substrate and the intermediate layer form a continuous layer. In addition, by adopting the aforementioned good method, a continuous layer is also formed for the intermediate layer and the hard carbon film. Consequently, in such case, a continuous layer is formed from the substrate to the hard carbon film. (JP '334, translation at p. 8).</p> <p>The reaction conditions for the hard carbon film forming region can be set according to the conditions when the hard carbon film is formed. Usually, the conditions are the same as the conditions when the intermediate layer is formed.</p> <p>The hard carbon film formed in this way may be either a diamond film or a diamond-state carbon film. (JP '334, translation at p. 9-10).</p>

'086 Patent	U.S. Patent No. 4,783,368 ("368 Patent")
<u>Claim 25</u>	
A hard-carbon-film coated substrate comprising:	<p>The '368 Patent was filed on Nov. 5, 1986, over one year before the U.S. filing date of the '086 patent.</p> <p>Elements below show hard carbon film.</p>
a substrate consisting of a metal or an alloy mainly composed of Ni or Al, or stainless steel,	<p>Preferable examples of a metal substrate employable in the present invention include, for instance, stainless steel; Cu; alloy of Cu and Al, Zn, Cd, Ge, Ti, Ag, Si and the like; Al; alloy of Al and Mn, Mg, Mg-Si, Si, Cu, Mg and the like; Ni; Zn; alloy of Zn and Pb, Fe, Cd, Sn, Al; W; Mo; and WC. Among these examples, substrates made of widely-used stainless steel, Cu, Cu alloy, Al, Al alloy, Ni, Zn, Zn alloy are preferable, because they are economical, easy to get, easy to work and moreover a substrate having large area can be produced with ease. ('368 Patent at 9:26-35)</p>
an intermediate layer mainly composed of carbon arranged directly on and in contact with said substrate; and	<p>The hard carbon film in the present invention can be formed as an interlayer on a metal substrate such as stainless steel in the thickness of 10 to 5000 Å, preferably 20 to 2000 Å, thereafter a carbon film containing substantially no element of group IVA can be formed thereon. ('368 Patent at 10:49-54.)</p>
a hard carbon film arranged on said intermediate layer.	<p>The hard carbon film in the present invention can be formed as an interlayer on a metal substrate such as stainless steel in the thickness of 10 to 5000 Å, preferably 20 to 2000 Å, thereafter a carbon film containing substantially no element of group IVA can be formed thereon. ('368 Patent at 10:49-54.)</p> <p>The above-mentioned hard carbon film in the present invention is generally made of diamond or diamond-like carbon. The surface Vickers hardness thereof is 500 to 10000, preferably 1000 to 10000, and more preferably 2500 to 10000. The insulation resistance is 10^2 to $10^{16} \Omega \cdot \text{cm}$, preferably 10^8 to $10^{16} \Omega \cdot \text{cm}$. The adhesive strength to the metal substrate is 5 to 200 kg/cm², preferably 20 to 200 kg/cm². The hard carbon film in the present invention is suitably used in insulated substrates for an electronic circuit, wear-resistant surface coating, and the like. ('368 Patent at 10:38-48.)</p>
<u>Claim 26</u>	

'086 Patent	U.S. Patent No. 4,783,368 ("368 Patent")
The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 8000 Å.	Though the thickness of the hard carbon film is not particularly limited in the present invention, the thickness of 10 Å to 100 μm, preferably 20 Å to 30 μm is considered to be producible, because the film is produced by a method using plasma or ions. ('368 Patent at 10:3-7.)
<u>Claim 27</u>	
The coated substrate of claim 25, wherein said intermediate layer has a thickness of from 50 Å to 4000 Å.	Though the thickness of the hard carbon film is not particularly limited in the present invention, the thickness of 10 Å to 100 μm, preferably 20 Å to 30 μm is considered to be producible, because the film is produced by a method using plasma or ions. ('368 Patent at 10:3-7.)
<u>Claim 28</u>	
The coated substrate of claim 25, wherein said hard carbon film is a film of diamond-like carbon.	<p>The hard carbon film in the present invention can be formed as an interlayer on a metal substrate such as stainless steel in the thickness of 10 to 5000 Å, preferably 20 to 2000 Å, thereafter a carbon film containing substantially no element of group IVA can be formed thereon. ('368 Patent at 10:49-54.)</p> <p>The above-mentioned hard carbon film in the present invention is generally made of diamond or diamond-like carbon. The surface Vickers hardness thereof is 500 to 10000, preferably 1000 to 10000, and more preferably 2500 to 10000. The insulation resistance is 10^2 to 10^{16} Ω·cm, preferably 10^8 to 10^{16} Ω·cm. The adhesive strength to the metal substrate is 5 to 200 kg/cm², preferably 20 to 200 kg/cm². The hard carbon film in the present invention is suitably used in insulated substrates for an electronic circuit, wear-resistant surface coating, and the like. ('368 Patent at 10:38-48.)</p>